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Metallurgical Physics

THE structure of the atom has been the principal subject of research of many physicists during the past two or three decades. In most cases, this research has been limited necessarily to isolated atoms. In fact, the analysis of the spectra of these atoms enabled Bohr to formulate a quantum theory of the structure of the hydrogen atom. Since then, advances have occurred steadily, until now our understanding of the structure of isolated atoms is fairly complete.

Until recently, however, little was understood of the structure of the closely packed atoms which make up a solid. The interaction of the neighboring atoms is such that the behavior of the outer atomic electrons is completely different from that in isolated atoms. Lately several papers have been published in which the foundation has been laid for a satisfactory theory of the structure of atoms in metals and other solids. Thus, an entirely new field has been opened up to the physicist. That he is intensely interested in this work is evidenced by the rapidly increasing number of papers on the metallic state and by the fact that in the past few months, two books concerned exclusively with the theory of metals have been published and another is promised shortly.

In this new field of endeavor, an excellent opportunity for cooperation between the metallurgist and the physicist is offered. The physicist naturally approaches this subject from the point of view of correlating the comparatively simple and well-known properties of electrons and free atoms with the complex properties of solids. The metallurgist, on the other hand, has made extraordinary progress in analyzing the maze of phenomenological data at his command and has transformed it into a relatively few important generalizations. The gap between these two approaches to the understanding of the metallic state can be bridged effectively only by full cooperation between the metallurgist and the physicist.

The possibilities of such cooperation were well shown by the success of the Symposium on Metals, held in Cambridge, January 28–30, sponsored jointly by the American Institute of Physics and the Massachusetts Institute of Technology. In the news section of this issue, a report of this meeting is given which shows the range of the papers covered. Many of the papers themselves will be found in this and succeeding issues of the *Journal of Applied Physics*.

THE EDITOR

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Moisture in Textiles, by A. C. WALKER

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Physical Basis of Color Measurement, by A. C. HARDY

Modern Theory of Solids. III, by FREDERICK SEITZ AND R. P. JOHNSON

Contributed Research Papers on the Reignition of an Arc, Flow of Fluids Through Porous Media, Transformations in Antenna Calculations, and Rheological Properties of Asphalts.

Some Physical Problems in the Electrical Power Industry

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IN attempting to write a paper on "Physics in the Electrical Power Industry," I find that my first task is to limit arbitrarily and quite artificially the meaning of the word "physics" in such manner and degree that my paper shall not reduce itself to the single statement "The electrical power industry is physics" and stop right there as a one sentence essay. In fact, the electrical power industry was born in the laboratory and mind of the natural philosopher or pure physicist, Michael Faraday, and its activity may be described as repeatedly and continuously, in large scale and small, and in the most varied manners, giving demonstrations of his law of electromagnetic induction. Magnetic field in iron links electric current in coil, in generator, motor and solenoid in endless profusion upon this earth. Great dams are built and momentous political issues arise, in connection with further repetitions of Faraday's great experiment.

In fact, unlike mechanical and civil engineering, electrical engineering did not exist at all, before the physicist, and the first electrical engineers were the great physicists—Weber, Kelvin and others. The common electrical units, the volt, ampere, ohm, henry, farad, watt, are all—with one exception—named after renowned physicists. Limiting ourselves to electrical power engineering, the pioneer dynamo designer, Hopkinson, turned to Kelvin for enlightenment on the forces on conductors in slots in iron, and the illustrious theoretical physicist and mathematician, Poincaré,[1] wrote an important paper on the magnetic energy in alternating current power systems.

Again, in fact, the subject matters of electrical engineering and physics are so closely interrelated that in 1898, the Physical Society of London and the Institution of Electrical Engineers collaborated in producing *Science Abstracts* with the subtitle *Physics and Electrical Engineering*, giving literature abstracts in both fields, issued first in single annual volumes.

So actually, in fact, with any reasonable interpretation of the word "physics," the "electrical power industry is physics" and I must extricate myself from my dilemma by imposing unreasonable and arbitrary limitations on what I shall mean by both "physics" and the "electrical power industry."

I shall begin by limiting the electrical power industry to the generation and distribution of electrical power, and exclude from consideration the utilization or conversion of electrical into other forms of power, as light, heat, electrochemical process. Although the development of such fields of application of electrical power is vital to the power industry and is its *raison d'être* I must exclude them because of the surfeit of examples of physics problems solved and unsolved which they would offer. I must also limit the electrical power industry to the distribution of electrical power at low frequencies; otherwise, I would invade the field of communications, which also distributes electrical power but at higher frequencies. My power industry stops where the power line enters the broadcasting station. I also make the mild limitation to generation of electrical power from mechanical power; that is, by means of relative motion of electrically excited parts of machines. This excludes from consideration batteries, photo-cells and other sources of low frequency power. I limit myself exclusively to the generation and distribution of alternating currents. Direct current transmission is still a thing of the future.

Now comes the more difficult matter of imposing limitations upon the meaning of "physics" so that what is left of the electrical power industry may also include some electrical engineering as well. Beginning with Faraday, it was all "physics." How much of this "physics" shall I say is now electrical engineering. I accomplish my task by examining textbooks on electrical engineering, and the state of knowledge on electrical matters of electrical engineering graduates. I find that the electrical engineering of the electrical power industry consists essentially of the macroscopic phenomenological treatment of electromagnetism of stationary and moving media; the field equations describing the interrelation of the various electromagnetic vectors and scalars, the equation for mechanical forces arising from the electromagnetic field, $F=eE+(1/c)[B\times I]$, and the supplementary equations of Maxwell relating the various electrical vectors in matter with material constants, $D=\epsilon E$, $B=\mu H$, $I=\sigma E$, etc., mostly developed for linear circuits, and illustrated by power machines, form the basis of almost all of the electrical engineering in texts and minds of engineering graduates. Hence, I shall say that all electromagnetic theory, where the properties of materials appear only as constants, such as permeabilities, conductivities, etc., shall now be regarded as electrical engineering, and only where an inquiry or problem goes more deeply into the nature of the electrical constitution of matter shall it be called physics.

It may be argued that in the case of the magnetic properties of iron at least, the engineer cannot be content with the simple descriptive constant, permeability, but must consider saturation and hysteresis as well. It is my intention, however, to use the notion of material constant in a more general sense, and to regard a family of hysteresis curves as giving the magnetic properties of a material in as superficial (although for most engineering purposes sufficient) a way as to be equivalent to the equation $B=\mu H$. It is only when an inquiry goes into such matters as the lattice structure of the iron, the spin of the constituent electrons, etc., that I shall regard it as "physics" and not "engineering."

Having thus limited the meaning of "physics," it seemed to me that I might discover the extent of "physics" in the electrical power industry and the activity with which it is being pursued, by examining the contents of the leading journals devoted to electrical engineering in this country and abroad for the past few years, and listing the titles of papers which clearly belong to "physics" in my restricted use of the term. However, after spending a few hours with the *Transactions of the American Institute of Electrical Engineers*, I found that this would be altogether too large a task. In the two volumes 53 and 54 for the years 1934 and 1935, I found seventy-seven papers which I had to classify as "physics." Of these, thirteen were educational in character, written mostly by physicists, and were not the initial publication of new work. It is significant, however, that so much space in a technical journal specifically for electrical engineers should be devoted to keeping the reader abreast of modern ideas and developments in theoretical physics. The remaining sixty-four papers are still a very considerable number and enable me to state that a large part of the research now going on in electrical engineering is research in "physics."

These sixty-four papers may be further classified as follows: electrical properties of vacuum involving principally motions of electrons and apparatus cooperating with same, 8; electrical properties of gases important to electrical engineering in such ways as in lightning, insulator flashover, arcs in circuit breakers, sparking under brushes, arc rectifiers, etc., 31; electrical phenomena in dielectrics dealing with conduction and breakdown conditions in insulating liquids and solids, 8; magnetic materials, 3; and miscellaneous subjects such as wetting of dielectrics, sound absorption, incandescence, 14. Al-

Dr. Slepian's paper is the last of the excellent group of papers presented at the Symposium concerned with Physics in Industry at the meeting of the Founder Societies of the American Institute of Physics in New York, last October. This paper, together with the other papers in this group, will be published shortly in book form by the American Institute of Physics.

though the two volumes of the *Trans. A. I. E. E.* selected may not be typical, it is fairly safe to conclude that a very large part of the "physics" research going on today in electrical engineering concerns electrical discharges in gases. Electrical properties of conducting materials are strangely

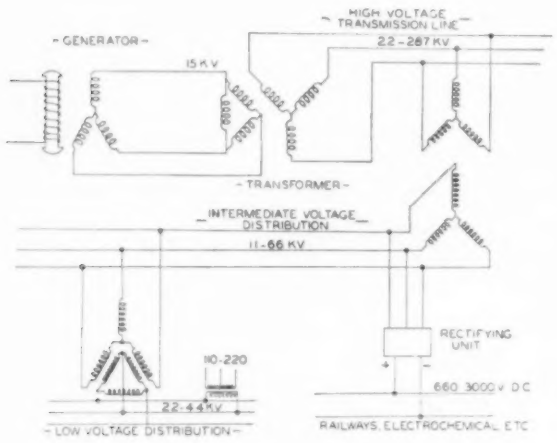

FIG. 1.

absent. The new developments in the theory of metals and semiconductors have as yet not affected the electrical engineer.

It is not surprising to find physicists in the electrical power industry working with electron tubes and low current gas discharge tubes using these devices as means for measuring and controlling the larger currents of the actual power processes. Much development of this kind has taken place and electronic regulators, controllers, timers and "what-nots" have been developed and are finding widening applications. Photocells and photo-tubes, popularized as the "electric eye" are being applied in most varied counting, sorting, detecting and controlling operations in industry. I prefer, however, in this paper to turn away from these more usual fields of the applied physicists and try to find my examples of physics in the more basic functions of the electric power system; namely, in the actual generation and distribution of electrical power, and not approach quite so close to the utilization circuits as in these more obvious examples.

Let us consider the single field which, in my study of recent literature, brought forth the largest number of papers, i.e., electrical properties of gases, and examine where and in what ways it forces itself upon the electrical power engineer. We see that electrical discharges in gases enter power systems at practically every point, beginning with the generator itself, and going down to the ultimate utilization circuits. Sometimes they appear as means for accomplishing useful purposes, sometimes as destructive agents causing failure of electrical apparatus. More often, the two roles of evil spirit and rescuing angel come together, as in destructive lightning, and the counteracting protective discharges in the spark gaps of lightning arresters or as in the highly desirable and necessary initial arc, which forms spontaneously at separating contacts in an opening switch, and the persisting arc which continues to play for many cycles between the already separated contacts.

The figures which I have prepared are intended to depict the numerous ways in which the electrical phenomena in gases affect a power system. The first is merely a diagram of a large power system. The generator, driven by steam or water turbine, produces alternating current, usually at about 15,000 volts. This voltage is then stepped up by transformers to a value suitable for transmission over greater distances, that is from 22 to 287 kilovolts. We then come to the intermediate high voltage distribution system for more limited distances at 11 to 66 kv. Then comes the quite local distribution system of 2 to 4 kv. Then lastly the domestic and industrial utilization circuits of from 110 to 600 volts.

Starting with the generator Fig. 2, we have the exciter, with a commutator and brushes for producing direct current for the field of the generator. But commutation, as we shall see,

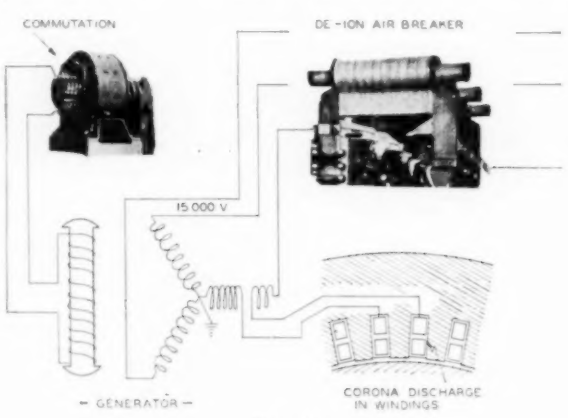

FIG. 2.

depends for its proper functioning upon a discharge between brush and receding commutator segment. The generator itself uses the electrical properties of gases only incidentally as air insists on intruding itself into the insulating system. Corona discharge in the minute air space between insulated coil and iron slot side is one of the most troublesome problems in generator design. We next come to the power switch, which functions by means of an arc between separating electrodes. I have indicated here a form of switch which uses a series of short arcs with cold cathodes whose possible existence was debated and established by physicists such as K. T. Compton,[2] H. Stolt,[3] and others.

Passing through the transformer, in Fig. 3, we come to the high voltage transmission system which frankly uses the insulating quality of air in its normal state. The bushing on the transformer must be designed so that the air about it under normal conditions is insulating, but it must also be of such construction that under abnormal conditions when excessive voltages obtain, the air about it will break down and conduct before the insulation within the transformer is endangered. Also, the discharge which forms must take a path not so close to the porcelain as to shatter it by its heat. Such complex problems of flashover around insulators have so far been handled only empirically, and a good physical theory is badly needed.

The oil circuit breaker uses the arc playing in a bubble of gas formed by decomposition of the oil. For high voltage work, means must be used to alter the shape and disposition of the bubble walls so as to make even a short arc capable of accomplishing its task of interrupting the circuit at an early current zero after separation of the contacts.

The transmission line itself runs out into the sea of air where takes place the spectacular high voltage heavy current discharge, lightning. Unfortunately, either by direct stroke, or inductively, the lightning becomes part of the transmission system and the engineer must cope with it with protective devices which, although highly developed, still do not give complete protection to electrical equipment. Lightning is still the principal cause of interruption of service on transmission lines.

The lightning arrester protects against the damaging discharge by producing a protecting discharge. Its spark gaps must initiate the discharge and also cooperate with the other element of the arrester in terminating the discharge after the lightning has passed. The major physical tool of the engineer for studying such problems is the physicist's cathode-ray tube, and the major conceptual tool, the physicist's theory of ionization in gases and particularly Townsend's theory of breakdown in gas spaces. The modifications necessary in Townsend's theory to meet the conditions of high pressure and high breakdown voltage have been worked on by various physicists, but the need for the modifications and their development and elucidation were first given by the engineer Rogowski[4] in a most brilliant and elegant series of researches in what

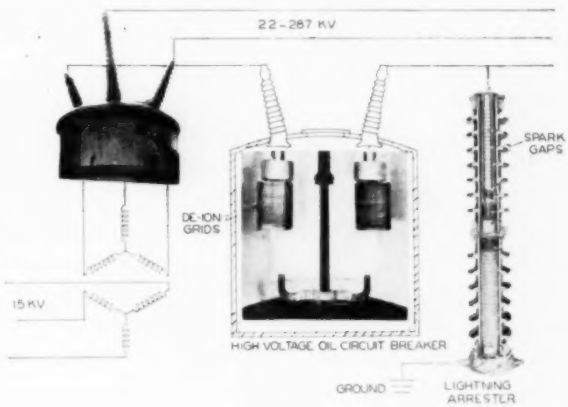

FIG. 3.

are quite definitely fields of theoretical and experimental physics.

Although the theory of the simple spark gap under laboratory conditions may be regarded as in a satisfactory state, the performance of spark gaps in lightning arresters still leaves room for considerable improvement. Enclosed in weather-tight porcelain containers, there is a variability and spread in the sparking voltage under various conditions sufficient to prevent a close adjustment to system voltage, and causing thereby a departure from the ideal protective performance desired. Shown in parallel with the insulating string in Fig. 4 is a new form of lightning arrester, the protective tube, which may be cheap enough to permit its wide use in trans-

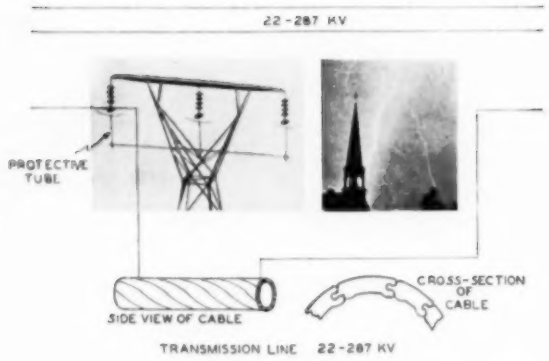

FIG. 4.

mission lines. Here a spark gap is cunningly devised so that its discharge passes down a fiber tube. The heat of the discharge decomposes some of the fiber into gas which passes through the discharge at such pressure and velocity as to extinguish the power arc at a following current zero. The problems presented here are to make the tube withstand the high pressures developed by the copious gas generation at high currents, while at the same time supplying sufficient gas to extinguish the arc at light currents.

The transmission line itself effects power flow in virtue of the magnetic and electric fields with which it surrounds itself. The latter must be so proportioned that the air is not over-stressed and made too conducting. The section of the conductor is determined principally by this requirement, and for economy of materials, hollow conductor arrangements are used. The economics of the situation require lines to be operated close to the limits at which a small corona discharge begins. Corona discharge from wires has been studied theoretically and experimentally by engineers and physicists, and a particularly complete theory has been given by R. Holm.[5] However, in dealing with conductors subjected to oxidation and weathering we must still depend on empiricism and closer predetermination of corona conditions is highly desirable.

The complete enumeration of the various examples of discharges in gases in power systems would become tiresome. Proceeding more rapidly, we see in Fig. 4, for the intermediate high voltage system the deteriorating effect of ionization in crevices in cables as the compelling reason for the thorough and painstaking impregnation, and a major reason for the development of cables in oil under pressure. We see power fuses, in which the action of the arcs in them is improved by the generation of gas from fiber walls, or steam from boric acid cartridges. We see mercury arc rectifiers converting alternating current to direct current, for railway industrial and electrochemical use. In the low voltage distribution system in Fig. 5, we see a transformer with built-in protector tube, somewhat similar in principle to the protector tube in the high voltage circuit. In the low voltage utilization circuits, we see arcs working in myriad pushbuttons, and controller switches, electrical discharges effecting the commutation in countless motors. Worth special mention is the low voltage distribution network system used in metropolitan areas, where faults in insulation are permitted to burn themselves clear, and where the resulting arc usefully interrupts the short circuit current.

Let us discuss in a general way these applications of discharges in gases in power systems, and find what problems are common to them. We see that in all of them there are problems of properly initiating the useful discharge, and also of properly terminating the useful discharge. For alternating current circuits, proper termination of the useful discharge usually means prevention of reinitiation after a current zero. Let us also consider how physical theory aids in dealing with these problems, and some points at which it fails.

The initiation of a discharge by high voltage breakdown has already been considered in the discussion of spark gaps in lightning arresters. Here the discharge is, so to speak, created full length. More often, in other applications, the cathode part of the discharge is initiated or set up, first, and the rest of the discharge follows spontaneously. Thus in low pressure gas tubes such as thyratrons and grid-glow tubes, a heated thermionic cathode provides that there shall be electrons available when proper voltages are applied to anode and grid. Langmuir's[6] theory of the formation of a plasma then satisfactorily accounts for the development of the discharge, but it is quantitatively worked out only for simple electrode arrangements. In the usual mercury pool arc rectifier also, the cathode is kept in an excited state by the maintenance of a

discharge to it from an auxiliary electrode or other main anodes.

After initiation, in most of the devices I am describing, there is usually no difficulty in maintaining the discharge, but in the low pressure gas tubes there is a curious limit to the amount of current which can be carried. When a limiting value of current is exceeded, the magnitude depending on the pressure, a kind of instability sets in, in which the discharge is repeatedly sharply interrupted and reestablished, but erratically, at no definite frequency, and with the development of high voltage in inductive circuits. Inasmuch as often it is this phenomenon which limits the rating of mercury arc rectifiers, this is a matter of practical importance. Langmuir and Mott-Smith[7] and Hull and Brown[8] associate this phenomenon with a high degree of ionization in the gas, and I venture the suggestion that a pumping of a high vacuum by the motion of the positive ions may be the explanation.

In the ignitron type of mercury arc tube, which is now finding industrial application, the discharge is initiated by an interesting application of the mathematical theory of steady current

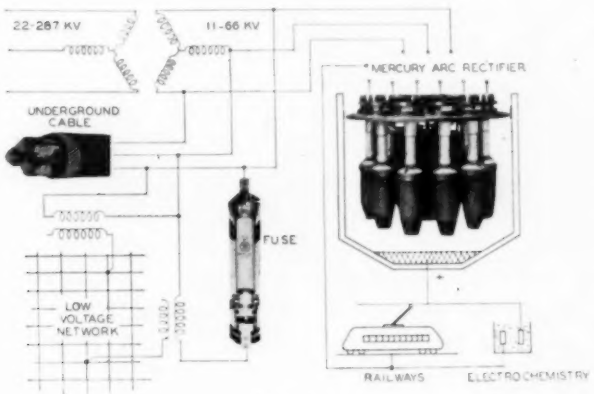

FIG. 5.

flow. By using a *stationary* rod of high resistivity material dipping into the mercury pool, it is possible to produce at the junction a concentration of electric field and current flow similar to that which occurs at *separating* contacts, and with a similar result, namely the formation of the cathode spot of an arc. In this type of tube no limiting current at which instability occurs has yet been observed, which is probably due to the anode being directly in the path of the vapor stream coming from the cathode spot.

The vapor coming from such a cathode spot at low pressures was observed by the engineer Tanberg[9] to have an extraordinarily high momentum and energy corresponding to more than a hundred volts. This should be of the utmost importance in a physicist's theory of the cathode of an arc. While some doubt as to the reality of Tanberg's high velocity stream was raised by Tonks,[10] Mason and Berkey[11] seem to have corroborated his result. A theory has been given by Risch and Ludi[12] involving very high degrees of multiple ionization of atoms.

It is quite evident that the initiation of the engineer's discharge requires him to know well the theory of the physicist's cathode, to deal with thermionic and high field electron emission, motion of electrons and ions, in fact to be physicist and make contribution to physics as in the Tanberg effect.

The initiation of the discharge in switches and on commutators takes place so simply and spontaneously by merely separating contacts, and the problem of terminating the discharge is frequently so difficult, that the useful function performed by the discharge is not generally appreciated, and the arc or glow is regarded as something evil, to be circumvented if possible. However, Faraday's law itself, upon which the very existence of the power system depends, would compel the development of disastrously high voltage if the current actually was suddenly reduced to zero at the moment of separation of the contacts. Only if the moment of actual separation of contacts is so closely synchronized with an alternating current zero that the electrostatic capacity of the system can absorb the momentary magnetic energy, will dangerously high voltage be avoided. But, generally, this electrostatic capacity is so small, that an impossibly high degree of synchronization is required. The kindly discharge in gas rescues the engineer from his difficulty. It permits him to separate his contacts when he will in the current cycle; the arc which spontaneously forms continues the current flow and effects the safe interruption of the circuit at a following current zero.

Attempts have been made to interrupt circuits

without a discharge by dispensing with separating contacts and introducing resistance which is increased continuously up to a practically infinite value. In fact the brush on commutator would seem to be an example of this, as the area of contact of brush and segment, and with it the reciprocal of the resistance introduced into the circuit being interrupted, approaches zero continuously as the segment moves under the brush. But analysis shows[13] that if the course of the resistance change is prescribed and if excessive voltage is to be avoided, there is still the necessity for a very precise synchronization

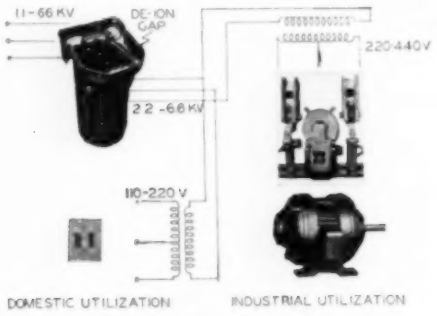

FIG. 6.

with the course of the current, and when as is practically always the case, the synchronization is imperfect, a rescuing discharge takes over or shares in the last conduction of current. If the synchronization is nearly enough perfect, the current in this discharge may be quite small, so that the discharge takes the form of a glow, which is nondestructive, and may be easily overlooked. I believe that in all successful and so-called dark commutation, a glow effects the last interruption of current.

It appears then that discharges in gases enter power systems not merely as annoyances or as conveniences, but in a certain sense are even indispensable for the existence of the power system itself. For the theorem of Poincaré teaches us that all the magnetic energy in an alternating current system so far as it is not balanced by a like amount of electrostatic energy, must be supplied by direct current circuits or commutating devices, and these last, when of any considerable power, depend on discharges in gases.

The termination of the useful discharge in alternating current circuits is usually reduced to the problem of preventing its reinitiation after a current zero. This may be accomplished by setting up conditions such that either the positive column or the cathode spot or glow cathode cannot reform themselves. In switches for higher voltage the positive column is worked with. Various means are used to compel the positive column to have so small a section at current zero that its temperature and degree of ionization fall to too low a value for reestablishment. Here, the thermal ionization theory of the positive column of K. T. Compton[14] is the guiding light. A recent excellent paper by Kesselring and Koppelmann reveals to what extent engineers need to go into the complex physics of heavy current arcs.

The means used for achieving the small positive column section are quite various. I may mention the solid barriers with restraining magnetic field in the "de-ion grid circuit breakers" of Westinghouse, the motion of oil under pressure in the "oil blast breakers" of the General Electric Company, the blast of gas in expulsion type fuses, and the gas blast switches used on the continent in Europe.

In low voltage switches and in higher voltage switches of the de-ion type, the absence of conditions necessary for formation of a cathode is depended upon. When the polarity reverses, if there is no thermionic activity at the new cathode, the discharge must take the form of a glow, at least initially, and if the available voltage is insufficient to maintain a glow cathode the discharge does not reform. However, with large current for stationary arcs, the voltage to reinitjate the discharge falls very considerably below the minimum glow voltage, and dependence must be made upon the positive column to assist in the interruption. No theory of this effect has been given. In switches of the de-ion type, the arc is kept in rapid motion over the faces of the anode and cathode, and this fall in reignition voltage is not obtained even up to very large currents.

In mercury arc rectifiers, ignitron, thyratron, grid-glow tubes and low pressure gas discharge tubes generally, the absence of a cathode spot and insufficient voltage to maintain a glow cathode are depended upon to terminate the discharge upon reversal of polarity. The low gas

pressure raises the voltage necessary to maintain the glow cathode, and so permits relatively high voltage to be handled. However, all these devices are subject to a type of failure, for which, in my opinion, no adequate theory has yet been given. Occasionally, and at random moments, in spite of the absence of conditions which present theory would regard as necessary, a cathode spot forms at a moment of incorrect polarity and causes a short circuit in the device. The statistical frequency of occurrence of these "arc-backs" or "back-fires" is such as to indicate that molecular aggregates comprising a few hundred thousand or million molecules are involved, which may be impurities on the electrode surface, or particles in Brownian movement, through the gas and coming into contact with the anode. However, a detailed theory of how such aggregates may cause arc-backs is still lacking.

The frequency of occurrence of these arc-backs increases very rapidly when thirty or forty kilovolts is exceeded, so that the problem of tubes of this type for very high voltage is still unsolved. Since the frequently discussed high voltage direct current power transmission must wait on these high voltage tubes, the phenomenon we are discussing is evidently of very great technical importance.

It is possible that working with the positive column or arcs at high pressure as is proposed by Marx[15] in his rectifier which uses gas blasts in a manner similar to European switches, may prove a better solution. However, it is not known, or at least has not been published, whether any phenomenon similar to arc-back will occur in such a rectifier. If the arc in a gas-blast switch occasionally reignites after a current zero, we merely have current flow for an extra half-cycle, which is a matter of little consequence, and would usually escape the attention of the operator. But in a rectifier, arc reignition means a short circuit, and interruption in the functioning of the apparatus. An abnormal reignition occurring only once in a million cycles would still be too often.

I believe I have made evident how one particular chapter in physics, electrical conduction in gases, crops out at every point in an operating power system. I hope I have also made clear how indispensable the theory developed by physicists has been in solving the related technical problems, and how engineers, turned physicists, have in turn further elaborated and developed the theory. I hope also that by giving examples where theory is still inadequate or lacking, and where the design and performance of apparatus is hampered by the failure of such theory, I have indicated the large opportunity for further work of the physicist and the physicist-engineer in the electrical power industry.

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Albert Sauveur

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THE arts of winning metals from their ores, of controlling their properties, and of fabricating them into desired forms, while ancient in their origins, had made slow progress until the 19th century. The many notable advances during the 19th century were purely empirical. There was no knowledge of the internal structure of metals, of the procedures that control that structure, and of the dependence of the properties of the metals on their structure. This was possible only with the development of the science of metallography.

In this country, metallography began in 1891 with the researches of Sauveur, and its development during the succeeding thirty-five years has been dependent to a notable degree on the researches of Sauveur and of the students he has trained. The retirement of Sauveur, last year, from the professorship of metallurgy and metallography at Harvard University marks the end of the great initial period of development of metallurgical science, with its resultant improvements in the metallurgical art, and the consequent enormous increase and diversification in metallurgical production.

Sauveur was born in Louvain, Belgium, in 1863 of French parents. His education was at the Athénée Royal, Brussels; in the School of Mines, Liège; and at the Massachusetts Institute of Technology, where he graduated in 1889.

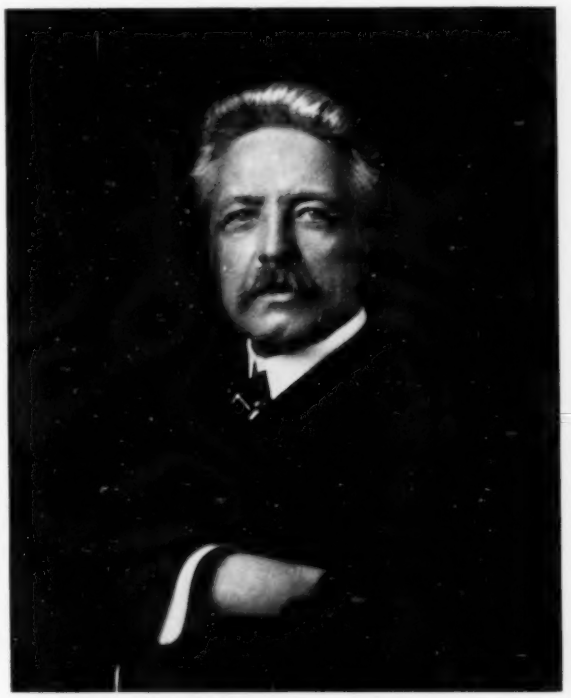
After two years in the laboratory of the Pennsylvania Steel Company, Sauveur accepted a position in the South Chicago Works of the Illinois Steel Company, then under the management of W. R. Walker. He was supplied with a crude upright microscope, with a fixed stage, and instructed to study the structure of steel. This appears to have been the beginning of metallography in the United States. Sorby in England had been using the microscope for the study of the structure of steel for some time but it was not until the presentation of his paper to the Iron and Steel Institute of Great Britain in 1886 that metallurgists became cognizant of this new procedure. They were naturally very skeptical as to the possibility of its yielding results of any value to the practical metallurgist. The 19th century was much less certain than the 20th century has become that there is a probable value in any scientific "baby." The only other notable investigators in this field before 1891 were Osmond in France and Martens in Germany. In 1891 all that had been done was to develop a method and to make observations; the correlations of these observations with the procedures in fabricating the steel and with the physical properties of the steel were as yet undetermined.

The South Chicago Works of the Illinois Steel Company was exclusively occupied, at the time, with the manufacture of Bessemer steel rails and, consequently, the attention of the budding metallographist was concentrated on this single product. It soon became apparent to him that the properties of steel rails were largely dependent on the dimensions of the microscopic constituents (the grain size) and that grain size was determined primarily by the finishing temperature. The prevalent view of makers of rolled products at this time was that steel should be worked at the highest possible temperature in order to minimize the power and the cost required to shape it. Sauveur demonstrated the existence of a critical temperature which yielded the smallest grain size after cooling, following hot work. These early results were described in a paper entitled "The Microstructure of Steel," presented to the American Institute of Mining Engineers at the Engineering Congress held in Chicago during the World's Fair in 1893. This paper was translated into French, German and Russian.

Three years later, on the basis of his continued researches, Sauveur presented a second paper, "The Microstructure of Steel and the Current Theories of Hardening," to the American Insti-

tute of Mining Engineers. This paper, together with the lengthy discussion which it provoked from English, French and American metallurgists, may properly be regarded as establishing the new science of metallography and as initiating a discussion of hardening which is still in active progress.

About this time the management of the Illinois Steel Company was changed; the new president was exclusively macroscopic in his vision. The laboratory which Sauveur had built up was discontinued and the investigator was given an undesired freedom. The new science was still too new to have penetrated the consciousness of industrialists and university presidents. Unable to establish industrial or university connections which would give him the opportunity to pursue his investigations, Sauveur decided to become a free lance. He opened testing laboratories in Boston and, with startling temerity, began in 1898 the publication of a quarterly paper known as *The Metallographist*. This paper, the first in its field, had great influence in creating an interest in metallography and lasted for seven years, during the last two years of which it was published monthly under the title of *Iron and Steel Magazine*. In the same period he published a fundamental contribution entitled "The Relation between the Structure of Steel and Its Thermal and Mechanical Treatment."



Albert Sauveur

In 1899 Sauveur joined the teaching staff at Harvard University (establishing there the first metallographical laboratory in any university) and retained that connection for thirty-six years. He was professor of metallurgy and metallography from 1905 until his retirement as professor emeritus in June, 1935. This whole period was fruitful in researches which have enriched his chosen field and established him in his outstanding position.

In 1912 appeared the first edition of Sauveur's celebrated book, *The Metallography of Iron and Steel*, the title of which was later changed to *Metallography and Heat Treatment of Iron and Steel*. This book, as the standard work in this country in its field, has gone through four editions with a total issue of over 19,000 copies. But Sauveur's zeal for his subject did not stop here. At the same time he started a correspondence course in metallography which, with its total enrolment of over 1500 students, has had enormous influence in disseminating a knowledge of the subject.

It is difficult to select from his 150 articles and papers dealing with the metallurgy of iron and steel those which are most significant. Perhaps the most important was the *Note on the Crystalline Growth of Ferrite Below the Normal Critical Range*, published in 1912, which ushered in the study of grain growth after cold work deformation and has been prolific in important results. His recent work on "age hardening" or "precipitation hardening," which is concerned with the mechanism by which age hardening occurs both in ferrous and in nonferrous alloys, is also a major contribution.

The current techniques in metallography owe much to Sauveur's inventiveness which has resulted in improvements in the inverted microscope and in the operations of polishing and etching specimens.

Sauveur was apparently the first person in the United States to make x-ray photographs. In January, 1896, a few months after Röntgen's discovery, he tried to apply x-rays to the detec-

tion of internal defects in steel but the crude appliances which were available to him proved inadequate for that purpose. This work was consequently discontinued.

Among his students and colleagues, Sauveur the man transcends Sauveur the scientist. Of distinguished appearance, always courteous, of a ready wit and a quick sense of humor, dignified, of quick perception and ready sympathy, he exemplifies well "the gentleman and the scholar." His writings are clear and well ordered and contain no suggestion that he is not writing in his native tongue.

As a teacher, he is beloved and revered by his students for the clarity with which he presents his material, for his fairness and patience, and for the courtesy with which he corrects their errors. A list of those men who have taken advanced work under him, and more especially those who have received doctorates for work under his guidance, reads like an honor roll of American metallurgists. The names include teachers such as Professors Mehl, Boylston, Krivobok, and van Wert, but, more particularly, research and consulting metallurgists, such as Zay Jeffries, H. C. Boynton, F. C. Langenberg, D. C. Lee, T. Fujihara, C. R. Wohrman, C. H. Chou, E. L. Reed, R. W. E. Leiter, H. E. Romine, M. A. Grossmann, R. H. Watson, C. H. Reinhardt, J. H. Hall, J. Winlock, and M. Yatsevitch.

Honors have poured thickly upon this pioneer and leader. Honorary doctorates have been bestowed on him by the Case School of Applied Science, Lehigh University, Harvard University, the University of Grenoble (France) and the University of San Marcos (Peru). The medals which he has received are the Bessemer Medal of the Iron and Steel Institute of Great Britain, the Elliott Cresson Gold Medal of the Franklin Institute, and the Albert Sauveur Achievement Medal of the American Society for Metals. This last award, of which Sauveur was the first recipient, is for pioneer metallurgical achievement after it has produced "a marked basic advance . . . in metallurgical knowledge." The orders which have been conferred on him by foreign countries are Chevalier, Legion of Honor (France); Officer, Order of Leopold (Belgium); and Officer d'Academie (France). Other honors include honorary memberships in societies both here and abroad, appointments to special lectureships, and United States delegate to international congresses, etc. The picture painted by these numerous honors is of a pioneer who has made good in such measure as to have commanded universal respect among his professional brethren and an admiration which sought to express itself in the bestowal of whatever honors are available for a metallurgist.

Now, having exceeded threescore years and ten, Sauveur, still young, and with undiminished powers, has abandoned the active pursuit of the profession of which he has been so long the ornament and is indulging in the luxury of philosophy. His latest book, *Metallurgical Dialogue*, written in a light vein, is a Socratic dialogue between master and pupil which sums up a great part of modern theory and knowledge of metallurgy (including the arguments for that will-of-the-wisp "beta iron") and incidentally introduces his ideas of education. It is the product of a mature mind, withdrawn from the fray, picking lightly from the stores of a life rich in creative thinking and in professional achievement.

When one hears it said that physicists have their feet off the earth, one should remember that their forerunners and their companions have made their empire of the earth. Or if one should come to feel that they are up in the air—in the metaphorical air, that is to say—one should not forget that they are of the same intellectual family as the men who have made the literal air a highway for going in the fastest possible manner from point to point of the ground, and even for exploring new territories of the ground.

—KARL K. DARROW, *The Renaissance of Physics.*
Courtesy of The Macmillan Company

The Spectrograph in the Iron Foundry

for

Rapid and Accurate Control Analysis

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Introduction

FOR many years the utility of the spectrograph as an analytical tool has been recognized. The discovery that a definite set of spectral lines is a characteristic of each element gave at once a means of determining the elementary constituents of a mixture, a qualitative application which has found considerable use in industry. The appeal of the method has lain in its high sensitivity and its ability to determine the presence or absence of many elements in one operation.

Almost immediately it was noted that if mixtures containing various small concentrations of an element are used in the light source, the spectrum due to that element varies in intensity with the concentration. It appeared that the composition might be determined, quantitatively, from the line intensity, and the spectroscope was hailed as the analyzer to replace all analyzers. The enthusiasm proved somewhat premature and applications led to disappointment. A satisfactory method of analysis needs not only sensitivity but repeatability, and in the early efforts this latter feature was deficient.

The first flurry of optimism, and the resultant chagrin, has been followed by a period of gradual improvement in technique. The contributions of such investigators as de Gramont[1] and Gerlach and Schweitzer,[2] encouraged further efforts to use the spectrograph in industrial problems. Numerous successful applications were made in the field of extremely small concentrations, where difficulties were experienced with the methods of chemistry[3] and where the demands for precision were not severe.

The use of the spectrograph for rapid and accurate quantitative analysis in the range of concentration from, say, one-tenth percent to five percent is a comparatively new development, and satisfactory technique has been worked out for only a limited number of elements in a few matrices.[4] At present, the spread of the use of the spectrograph in industry is handicapped by the past disappointments arising from the operations of those who have induced industries to try methods of questionable value. The failures have, it is feared, invested the spectrograph with a bad odor which should attach rather to the individuals who have introduced dubious technique in a field where continuous reliability is demanded.

In developing a satisfactory technique for the use of the spectrograph in analysis, special emphasis must be placed on the reproducibility of results—sensitivity is, in general, inherent. The work reported here has been directed almost wholly toward the improvement of reliability, and has resulted in a successful industrial installation.

The Analysis Problem

During the summer of 1934, the department of engineering research of the University of Michigan undertook to develop for the Campbell, Wyant and Cannon Foundry Company of

* Department of engineering research.
† Department of physics.

Muskegon, Michigan, a spectrographic method for the analysis of alloy cast iron to determine the elements chromium, copper, manganese, molybdenum, nickel and silicon. The analysis was to provide a production control and not a means of inspection of a finished product. The operation of the foundry is a continuous process in which the level of molten metal is maintained nearly constant in the cupolas by fusion, and in the electric furnaces by additions from a cupola. Ladles of molten iron are drawn off periodically for casting. It was proposed to analyze samples from the ladles, and to post the results as soon as possible, so that drifts in composition might be corrected before they exceeded commercial tolerance. This problem was placed with the authors in the department of physics.

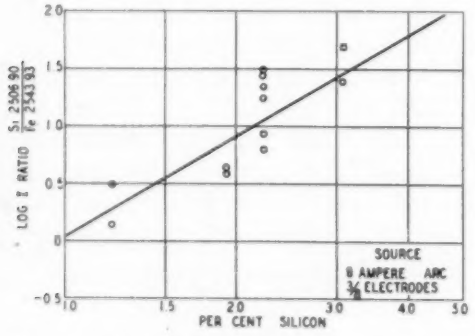

FIG. 1. Analysis with a small open arc. The relative intensity of the selected lines is plotted against the silicon content for several spectra made with the same sample of iron. The six repeats made at 2.2 percent show wide variations, indicating that analyses made with this source are quite unreliable.

It was hoped to develop a method of analysis of a reliability equal to or exceeding that of routine analysis in the chemical laboratory. The elapsed time between the sampling of the iron and the posting of results should be much shorter than that needed for gravimetric chemical methods. The cost of operation should be small, so that analyses might be made more frequently without increasing laboratory expenditures. It has been found possible to realize all these expectations, but it has been necessary to recognize and overcome numerous difficulties.

The accuracy demanded necessitated that the method be completely instrumental with nothing left to the guesswork euphemistically termed "estimate." The speed required provided no time for cumbersome methods such as those using numerous spectra made from electrodes soaked in solutions. Samples cast directly from the alloy in the pouring ladles have been used throughout. In the matter of the cost of operation, efforts have been made to avoid the use of unreasonable quantities of photographic material, while the high speed attained keeps the expenditure for operators at a very moderate level. Personnel is discussed below.

Instruments

The early work on this problem was beset with many difficulties. It soon became apparent that the reliability of the work would not exceed that of the instruments employed in the processes. At first, the microphotometer used for instructional purposes was used for analysis work also, but it soon showed itself unreliable to such a degree that its readings were useless for precision work. It was remodelled and its operation improved. It was still necessary, however, to provide a density measuring instrument suitable for use at the foundry.

Microphotometers available on the market did not appear entirely satisfactory for a number of reasons. A density comparator was supplied on memorandum through the courtesy of the Bausch and Lomb Optical Company of Rochester, New York, and with their cooperation, this was developed into a microphotometer of the required speed and accuracy. A new Littrow spectrograph purchased from the same company to replace the old model used in the early work proved to have excellent optical characteristics. Some improvement in its baffle system was needed to minimize internal reflections.

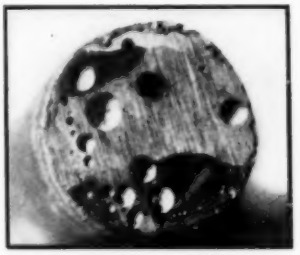

FIG. 2. The end of an electrode burned in a direct-current arc showing evidence of subsurface boiling.

Light Sources

Small d.c. Arcs

However, the principal problem was always the source to be used for the vaporization and

excitation of the alloy. Small direct-current arcs were tried with cylindrical electrodes cast in permanent molds. These electrodes were three-eighths inch in diameter and the arc currents ranged up to eight amperes, beyond which point molten material dripped from the electrodes. Results were not encouraging, as may be seen from the typical observations shown in Fig. 1.

Here, as in other methods involving internal control, analysis is to be performed through establishing, by the use of samples of known composition, the percentage content of an alloy as a function of the relative intensity of selected lines arising from the element and matrix, respectively, and using this relationship to evaluate the composition of samples of unknown content. Obviously, it is imperative that the functional relationship be monotonic so that the correspondence between relative intensity and percentage content is unique. When a single sample yields successive values of relative intensity of such divergence as those shown in the figure, the correspondence is far from unique and gross errors may be anticipated.

Several possible reasons for the inconsistencies experienced with the small open arc present themselves. A picture of the end of an electrode used in an arc is shown in Fig. 2. The slag has been ground away to expose the underlying metal, and it is clearly indicated that subsurface boiling may occur. This would lead to a random area of disengaging surface, and no equilibrium could be established. Since the arc was open, fluctuations in ambient conditions might influence the electrode and discharge temperatures. There is also the possibility that the composition of the sample varied from point to point, and that the portion burned was not representative.

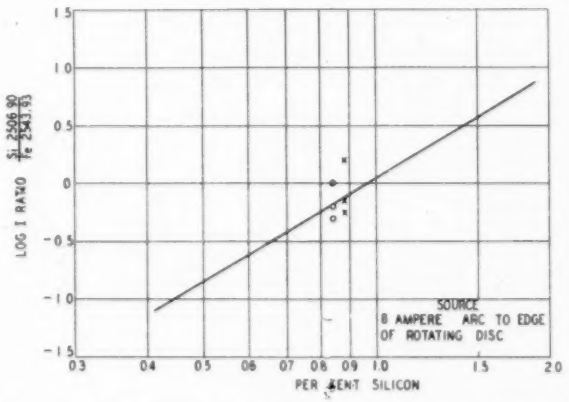

FIG. 3. Sampling by a slow continuous motion of the material under investigation. The reliability of analyses made with a small arc is little, if any, improved by these means.

It appeared that any or all of the conditions mentioned above might influence the results obtained, and it was decided to try some modification. The obvious way to minimize the effect of variation in composition is to burn up a sufficient amount of the material during analysis, but it immediately became apparent that inconveniently large currents would be required to vaporize any considerable quantity of iron. It was decided to try sampling the material under analysis.

FIG. 4. Arc for sampling material in a molten form. The illustration shows the driving motor, the electrode spindle and the adjusting lever in the hand of the operator. Continuous adjustment of the electrode is necessary to maintain the arc length.

Tests of repeatability were made on an arc between a pencil of graphite of spectroscopic purity and the edge of a cast iron disk rotated at a slow constant speed, such that it made slightly less than one revolution for each exposure. The results of this test are shown in Fig. 3. It appears doubtful that any improvement was effected.

Large Sampling Arc

Efforts made to sample the iron in a molten state resulted in the apparatus shown in Fig. 4. A relatively large arc was maintained between a cathode of graphite of spectroscopic purity and a three-eighths inch cylinder of the cast iron to be analyzed. The arc was vertical, with the negative electrode above the positive. The anode was rotated by the motor shown at the right. As the

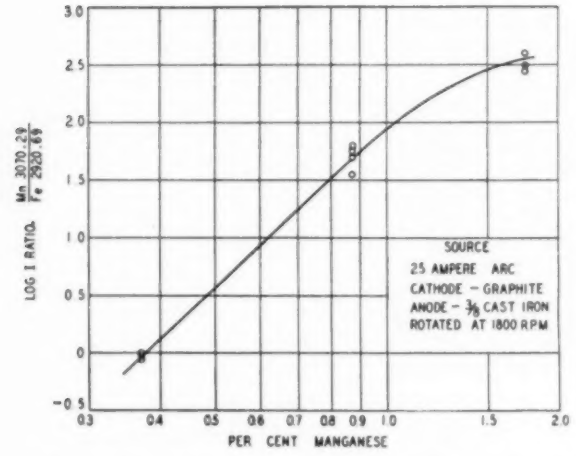

FIG. 5. Results obtained with arc shown in Fig. 4. Four readings are plotted for each sample. The improvement in constancy of the log I ratio may be noted by comparison with Fig. 1.

iron melted, it was forced outward by centrifugal force, and escaped from the edge of the anode in small drops. About two inches of the length of the casting was consumed per minute, and it was necessary to feed the anode slowly into the arc to maintain its length. It was difficult to enclose the arc and maintain the required visibility while, if the drops of molten iron were permitted to fly about, the destruction to trousers was considerable. The box shown in the illustration represents a scientific advance over the traditional barrel.

Typical results obtained with this arc are shown in Fig. 5, where four readings are plotted for each sample. It is readily observed that the new source shows considerable improvement in precision over the small stationary arc. It may be that the improvement is due in some measure

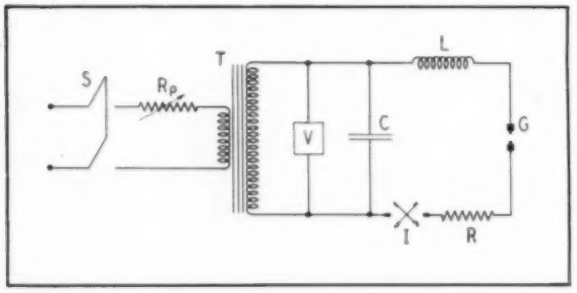

FIG. 6. Circuit diagram of condensed spark source, comprising S, line switch; Rp, adjustable primary resistor; T, high voltage transformer; V, electrostatic voltmeter; C, condenser; I, synchronous interrupter; R, resistor; G, sample gap; L, inductance.

to the sampling action which permits the consumption of fairly large quantities of the alloy, but more recent experiments indicate that the homogeneity of the iron is very good. It is thought that the benefit arises largely, if not wholly, from the tendency of the equilibrium, established between viscosity and centrifugal force, to maintain a constant temperature at the surface where the evaporation takes place, and, hence, a more constant vapor pressure in the discharge.

The accuracy of the analyses which could be performed with this arc was not ideal, but might be sufficient for the problem in hand. However, all the lines available and resolved for the important element, silicon, showed saturation at percentages lower than the normal content of several of the irons. The obvious solution of this

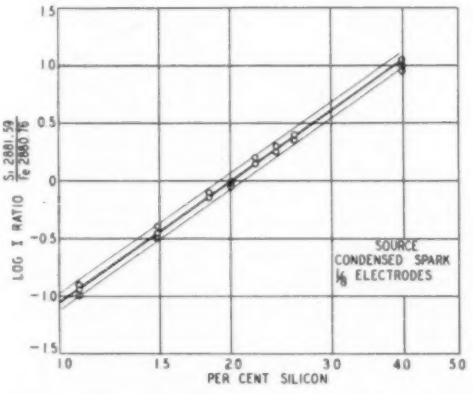

FIG. 7. Graph of results obtained with the spark source shown in Fig. 6. Four readings are plotted for each sample, the outer lines showing variations of ±5 percent of the amount of silicon present.

problem appeared to be dilution of the alloy before analysis, and samples were cast in tubes of Armco ingot iron. This material is so nearly pure iron that it was thought that the probable variation in its content of the elements under investigation would contribute no difficulties.

The tube and cast core were burned together with results as consistent as those shown in Fig. 5, and the relative intensity of the silicon lines was reduced. The saturation point, however, remained virtually unchanged. It is not quite certain why the dilution failed so completely to produce the desired results. Among the effects to be considered are the higher melting point of the ingot iron, and the possibility of

reduction in cross section of the part of the arc column containing silicon.

Other difficulties were experienced also. If the arc was to carry a fairly large current, it appeared desirable to use graphite for the upper electrode since it produces few lines and has no liquid phase to cause dripping. When a new rod of graphite was installed in the arc the relative intensity of a fixation pair—an arc line and a spark line—would fluctuate erratically, and no reliable analysis could be performed. Numerous methods of treatment of the graphite were tried, but none was thoroughly satisfactory. Continued use of the graphite in the arc would eventually put it in a condition such that the results would be repeatable.

The Spark Source

While the reliability of the rotating arc might be made satisfactory, it did not permit analysis for silicon over the required percentage range. Several other types of source were set up and tested briefly. Among these was a source described by Feussner,[5] for which he claimed a high degree of accuracy. The precision was found to be, in fact, quite good, but, in view of the complexity of quenched gaps and multiple resonances involved in the circuit, it did not seem certain that the apparatus would maintain its reliability over long periods of routine operation with infrequent checks. The results obtained with the Feussner spark, which burned a very small amount of material, indicated that the lack of homogeneity in the sample would not be a major problem, so it was decided to attempt to construct a spark source of such simplicity that reliable operability over long periods might be anticipated.

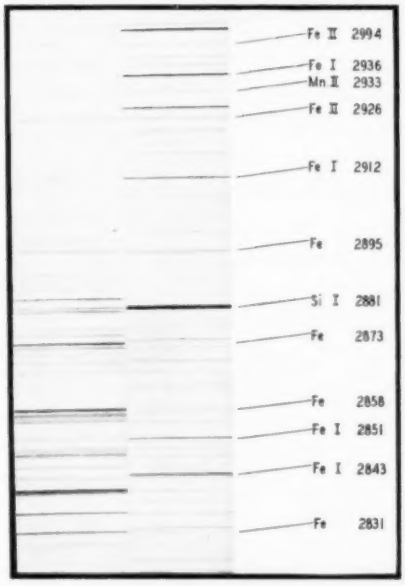

FIG. 8. Change of relative intensity of spectral lines with discharge temperature.

These efforts resulted in the apparatus shown in Fig. 6. The transformer charges a condenser which discharges through a series network comprising a synchronous interrupter, a resistor, an inductance, and the sample gap. The peak voltage imposed is 40,000 volts, and the elements are balanced to produce the lines desired at suitable intensities. The results obtained have been uniformly gratifying. A typical set of analyses for silicon is shown in Fig. 7, where four independent determinations are plotted for each sample against a careful analysis by the best chemical means. The outer lines indicate errors in analysis of plus and minus five per cent of the amount present. It may be noted that, in the working range of from one percent to three percent of silicon, all values fall within these outer lines. Likewise, in routine operation at the foundry it has been found possible to maintain a limit of error certainly not exceeding plus or minus five percent of the amount present.

The possibilities offered by the spark source in the control of relative intensities and saturation of lines make its use highly desirable. Spark spectra, taken of iron containing silicon, are shown in Fig. 8, where the silicon line at 2881.59A is easily recognized. Both spectra were taken from samples of identical composition, but at different discharge temperatures. For the upper spectrum, a large inductance was used in the discharge circuit, while the lower spectrum was taken with a much smaller inductance. The variation in the strength of the silicon line is quite apparent in the illustration, and since intermediate values of intensity are obtained at intermediate temperatures of the discharge, control of relative intensities may be effected over wide limits.

With a suitable selection of spectral lines the apparatus proved capable of effecting analysis for the six elements required, the following ranges of composition being covered simultaneously in a single spectrum: Cr, 0.10 percent to 1.00 percent; Cu, 0.20 percent to 0.80 percent; Mn, 0.40 percent to 1.00 percent; Mo, 0.10 per-

FIG. 9. The source room. The spark source operates from the power lines through a motor-driven voltage regulator. Controls are seen in the background. The sample gap is protected by a cover operating a safety switch.

cent to 1.50 percent; Ni, 0.15 percent to 1.25 percent; and Si, 0.50 percent to 4.00 percent. These ranges do not include all compositions for which analysis could be made with the lines chosen, but only those portions of interest to the problem in hand. Analyses for all six elements could be performed for most of the irons but for a few alloys containing larger amounts of copper and nickel the necessary percentages were not covered. More recent work detailed below has resulted in extensions to include all compositions of current production.

The Foundry Laboratory

Routine analyses are made at the foundry in a laboratory especially constructed for spectrographic work. The floor plan and views of the equipment are shown in Figs. 9, 10, 11 and 12.

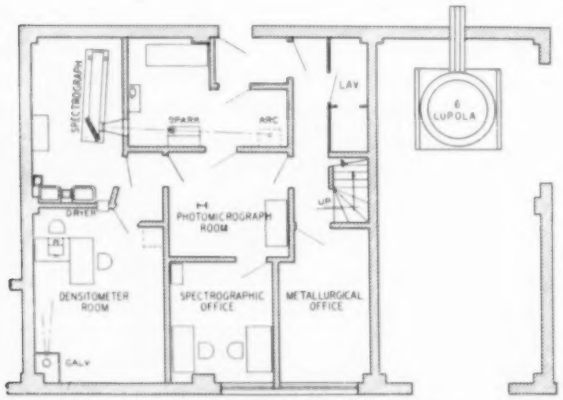

FIG. 10. The spectrographic laboratory at the Campbell, Wyant and Cannon Foundry Company. Note proximity to the line of furnaces whose output is analyzed.

The spark apparatus, built in the instrument shop of the university, is capable of handling a sample per minute. The pencils of iron to be analyzed are loaded into the spark gap in a jig which expedites accurate positioning. A trap with a safety switch covers the sample gap, and all other high voltage parts are enclosed in the housing. A voltage regulator, shown in the background, eliminates excessive fluctuations of line voltage. The convenience of design and arrangement of the spark equipment contributes materially to the high speed attained in the analysis.

FIG. 11. The darkroom. The inclusion of the spectrograph in the darkroom saves many steps.

The inclusion of the spectrograph in the darkroom saves many steps, and conveniences such as oscillating trays and a hot-air dryer are supplied to hasten the processing.

As has been stated, the microphotometer used is a remodelled Bausch and Lomb density comparator. The resolution has been decreased and a new photo-cell installed to permit the use of a critically damped galvanometer having a period of two seconds. The galvanometer, on a Julius suspension, is protected from drafts by the chimney shown in the background. New parts have been added to the plate carriage to permit motion from one spectrum to another without loss of proper alignment of the plate. Reading is greatly facilitated by a slow motion, comprising a worm drive, which engages the original rack and

pinion motion through a clutch. The clutch may be thrown out for rapid motion between readings. Readings may be made of the opacities of five or six spectral lines per minute, with an error not exceeding one percent at normal densities.

The laboratory has been in operation for about a year and its general arrangement has been found to be very satisfactory. Less than two man-minutes elapsed time is required per analysis, if spectra of eight samples are recorded on the same photographic plate. Experience at the foundry indicates that similar analyses in the chemical laboratory would entail three times the personnel charge.

Reliability

The question of precision in analysis is of fundamental importance and no pleas including the well-worn "lack of homogeneity" serve to make useful for production control a method of analysis which will not indicate very nearly the same composition if the sample is run a second time.

The reliability demonstrated by the condensed spark source in laboratory tests has been shown in Fig. 7, a graph of results obtained on samples analyzed chemically by the best analytical methods by expert analysts. The comparisons about to be presented do not stand on such a complete scientific basis. It is true that during several months of operation numerous check readings between chemical and spectrographic analyses have been obtained. Samples to be analyzed in both laboratories are supposed to be poured from the furnace at the same time, but it is not possible to guarantee that the two laboratories had in all cases samples of exactly the same composition. The comparisons are with routine-control chemical analysis which is, perhaps, somewhat more hurried than the best analytical determinations. In general, the press of arrival of new samples prohibited efforts to compose small differences in analysis. However, if the discrepancies were sufficiently great, one laboratory or the other might find time for a check run.

FIG. 12. The microphotometer equipment.

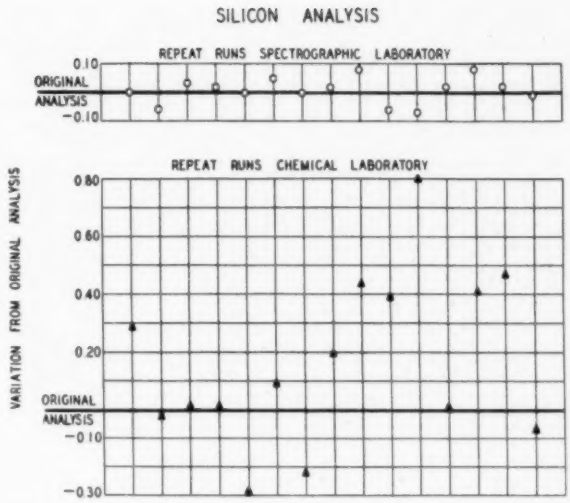

FIG. 13. Comparative reliability. Production records at the foundry indicate that the spectrographic analysis is more reliable than analysis performed in the chemical laboratory. The original analysis is the heavy line, and repeat analyses, the points shown. The silicon content is in all cases about two percent.

Fig. 13 shows a comparison of original and repeat analyses for the chemical and spectrographic laboratories at the foundry. The readings shown here include, with no omissions, all the repeat runs made on silicon analysis in certain types of iron during the period March 1 to May 20, 1936. The original analyses lie on the heavy line and departures of the repeat analyses from the original are shown by the distribution of the points. The silicon content is, in all cases, about two percent, and it is apparent that no repeat spectrographic determination differs from the original by more than eight points, or four percent of the silicon content, and that the

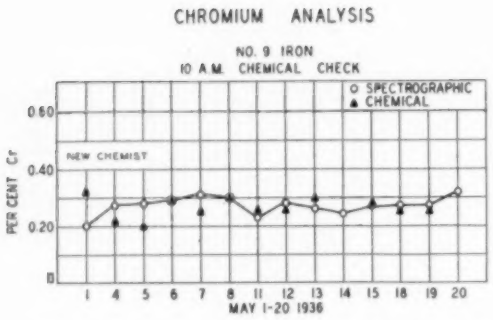

FIG. 14. Comparison of spectrographic and chemical analyses. New analyst at first of month shows rapid improvement in accuracy.

limit of error from the mean does not exceed plus or minus two percent of the amount of the element present. It is thought that a limit of error of plus or minus five percent of the content is sufficiently liberal to include such systematic errors as may be anticipated. It is important to note that this is an unselected list of repeat analyses from an actual routine-control installation, that it covers an elapsed time of nearly three months and is not a quotation of results obtained on a single photographic plate in a development laboratory.

The repeat runs made in the chemical laboratory for the same element and the same irons over the same period show considerably wider departures. This graph does not, of course, represent the average chemical accuracy, since check readings were taken only in cases where the initial determination appeared questionable, either through failure to check the spectrographic result on the same sample, or because the composition appeared to differ from the expected value. Perhaps the best view to take of this figure is that the departures show the relative probability of something's going wrong with the method. In any case, the spectrographic determinations show superior reliability. The analysts in the spectrographic laboratory previously worked in the chemical laboratory so the difference in personnel is negligible.

Figs. 14 to 19, inclusive, show a comparison, for each of the six different elements, of routine spectrographic and chemical analyses performed on irons in production at the foundry. In general, analyses were made in the spectrographic laboratory at much more frequent intervals than in the chemical laboratory. The figures show all chemical results posted, and the corresponding values obtained by the use of the spectrograph. The period selected for comparison is random and covers a sufficient time to be representative. The graphs show small differences in analysis but none of important proportions. It must be borne in mind that the exact composition is not known and that it cannot be guaranteed that the samples were of precisely the same composition. In view of Fig. 13, which demonstrates relative repeatability, and Fig. 14, which shows the beneficial effect on the chemical laboratory of spectrographic treatment of new analysts, perhaps no large part of the small variations

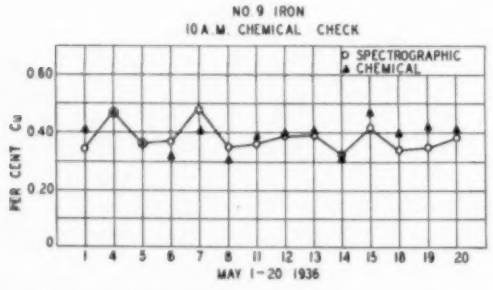

FIG. 15. Comparison of spectrographic and chemical analyses of copper. Segregations, which cause considerable difficulty in the chemical analysis of this element, are avoided by the high chill of the cast used for spectrographic analysis samples.

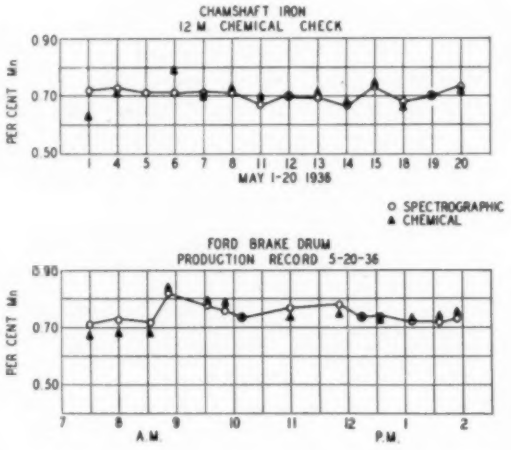

FIG. 16. Comparison of spectrographic and chemical analyses for manganese.

observed should be assessed as errors in the spectrographic determinations.

Errors may creep into chemical analysis in many ways, one of which is illustrated in Fig. 20. At 8:30, 10 and 1 o'clock the chemical analysis showed a high silicon content, which was not verified by the spectrographic laboratory. During the analysis of the 2:30 sample it was noticed that, in the silica to be weighed, there were several pieces of surface scale. These were removed with, perhaps, some silica adhering, and the result was a bit low. A more careful repeat on the samples, which had originally shown high silicon, agreed very well with the spectrographic values. Other cases could be cited.

It has been demonstrated that, in the hands of routine operators of the class customarily used in chemical laboratories, the spectrographic technique developed by the authors has shown a high degree of reliability. The whole process is instrumental and does not require continuous concentration on all details as do chemical methods. This may account for the fact that it appears to be continuously reliable, and entirely free from even occasional gross errors.

The claims of spectroscopists in development laboratories sometimes fail to be realized when routine operation in a manufacturing plant is attempted. It is hoped that it has been made adequately clear that the analyses shown in Figs. 13 to 20, inclusive, were taken from the production records of the Campbell, Wyant and Cannon Foundry Company and represent actual results obtained in an industrial spectrographic laboratory doing industrial work.

New Developments

As a result of recent work on the system of analysis, several changes are being instituted at this time. While no data under routine operating conditions are available, tests at the university laboratory indicate that the alterations proposed will extend the percentage range over which analysis may be effected, expedite the work, and yield improved accuracy in the determinations.

Changes in source temperature and the choice of a new set of spectral lines have led to the extension of the analysis range, so that the following percentages may be read simultaneously from a single spectrum: Cr, 0.01 percent to 1.50 percent; Cu, 0.20 percent to 3.00 percent; Mn, 0.30 percent to 1.25 percent; Mo, 0.07 percent to 1.50 percent; Ni, 0.15 percent to 2.00 percent; Si, 0.50 percent to 4.00 percent. All the irons in current production by the company

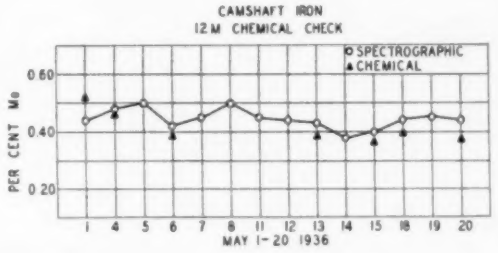

FIG. 17. Comparison of spectrographic and chemical analyses for molybdenum.

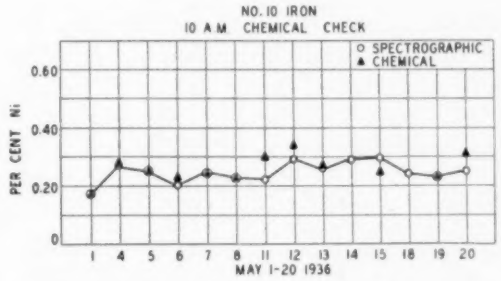

FIG. 18. Comparison of spectrographic and chemical analysis for nickel.

fall within these ranges and it is thought that further extensions are easily possible.

Through the cooperation of Dr. C. J. Staud of the Eastman Kodak Company of Rochester, New York, tests have been made on a number of types of photographic plates to determine their suitability for this work. The type 144–0 plate has been chosen to replace the polychrome plate previously used. Numerous experiments have been made on processing solutions to reduce the time which must elapse between the completion of the exposure and the beginning of microphotometer readings. It now appears possible from the dry exposed plate to produce a dry processed plate in less than nine minutes. For a given change of composition of the alloy the change in microphotometer reading has been increased two to threefold. The reproducibility of relative opacities appears as good as before and further increases in accuracy are indicated.

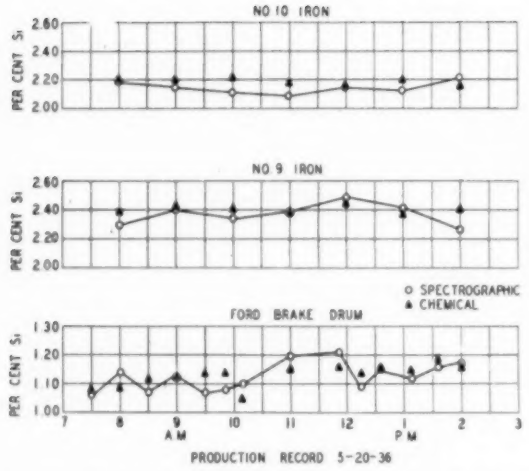

FIG. 19. Comparison of spectrographic and chemical analysis for silicon.

The methods of handling the various processes involved in an analysis have passed through several phases. Mention in detail of these processes has been postponed to this point since it was felt that only the most recent need be described. The samples used are cast in a permanent mold from the molten iron tapped off from the furnace. The form of the sample is cylindrical, one-eighth inch in diameter by one inch long. Electrodes of this small size have been found convenient and rapid to handle; the intense chill of the casting discourages segregation and equilibrium in the source is established almost instantly. Two sets of clamps hold two such cylinders in vertical coaxial alignment, the nearer ends being separated by one-quarter inch. The discharge crosses this quarter-inch gap and produces the light to record the spectrum. While the adjustment of the gap length is not at all critical, a loading jig is used for speed and convenience.

No condensing lens is interposed between the source and the spectrograph slit. The use of such a lens has not appeared desirable for a number of reasons; additional equipment involves additional hazard of variation in adjustment; the source produces sufficient light to record a spectrum in less than one minute, so no important saving of time could be accomplished; small variations in the position of the spark may lead to important errors if the spark is imaged on the slit.

A section of the spectrum extending from about 2220A to 2950A is recorded on a photographic plate eleven and one-half inches long in a special plate holder constructed in the physics instrument shop. The demands for speed in the operation of the microphotometer make desirable the production of a spectral line of appreciable area; a slit width of seventy microns and a line length of seven millimeters are used. Nine spectra may be recorded on a four-inch plate with sufficient separation and margin, while the precision is such that only one spectrum is required for the analysis of each sample.

Calibration

The photographic plate is processed and, when dry, is installed in the microphotometer. Attempts to read wet plates have been uniformly discouraging. Readings are made of the opacities of several selected lines due to the matrix, in this case iron. Arbitrary values of exposure have been assigned to these lines in such a way that if the lines are of moderate densities a plot of galvanometer reading against log exposure is linear. The selected line due to the element to be analyzed is measured, and the log of the ratio of its equivalent exposure to that of a selected iron line is read from the arbitrary scale mentioned above. This is done with a graduated set of samples whose compositions are known from careful chemical analysis, and the relation between log exposure ratio and percentage content is established. At this point the standard samples may be laid aside, and need be used further only for occasional checks. To analyze a sample of unknown composition, the log exposure ratio is determined as above,

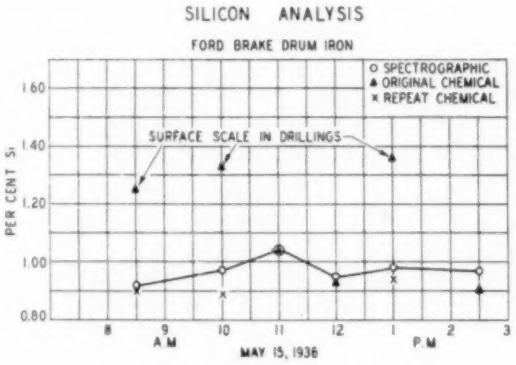

FIG. 20. An error in chemical analysis.

and the percentage content of the element is read from the curve of their relationship.

It is apparent that the method involves internal control with interpolation between lines of the matrix, and, hence, follows directly the suggestions of Gerlach and Schweitzer. Obviously, other methods of interpolation might be used with equal success: no especial virtue is claimed for the one outlined above except that it appears direct and effective. If several spectra are recorded on a single plate, it is considered necessary to read the whole set of matrix lines for the first spectrum only. For succeeding spectra, the opacity of the whole set of lines is known from reading any one of them.

Six analyses may be performed, to determine the percentage content of the elements mentioned, on a single sample in fifteen minutes elapsed time. Normally, spectra for forty-eight analyses on eight samples are recorded on each plate and the posting of results may be completed in thirty-five minutes. The speed and precision attained has exceeded expectations. Operating expenses are very reasonable, and the personnel demand small for the number of analyses performed. The technique developed is capable of extension to many other elements and matrices, if such extensions are, or become, of interest to industry.

Summary

To obtain the rapid analysis necessary for rigorous composition control in routine production, satisfactory spectrographic technique has been developed, and an installation put in operation in a large Michigan foundry, which produces alloy cast iron. Spectra are recorded, on a photographic plate, from the condensed discharge across a one-quarter inch gap between the ends of two cast cylindrical electrodes one-eighth inch in diameter. After the plate has been processed and dried, opacity measurements of selected lines are made on a microphotometer, and the percentage composition is read from calibration charts. The condensed-spark source developed in this laboratory gives excellent reproducibility. Its principal features are the control of the damping in the oscillatory circuit, and the use of a synchronous interrupter to maintain the discharge potential. The normal speed of recording spectra is one sample per minute. A suitable choice of photographic emulsion and of processing solutions and technique permit the processing and drying of the plate to be completed in slightly less than nine minutes. The microphotometer has been remodelled for rapid operation, and permits the measurement of five to six spectral lines per minute. Calibration is effected by the use of a series of samples of known composition, the relative intensity of lines due to element and matrix, respectively, being plotted against percentage content in accordance with internal control methods. Analyses for six elements are obtained from a single spectrum, the percentage ranges covered being as follows: Cr, 0.01% to 1.50%; Cu, 0.20% to 3.00%; Mn, 0.30% to 1.25%; Mo, 0.07% to 1.50%; Ni, 0.15% to 2.00%; and Si, 0.50% to 4.00%. Other ranges may be obtained by variation of the discharge conditions. Six analyses for a single sample may be completed in fifteen minutes; or if spectra of eight samples are recorded together on a plate, the forty-eight analyses may be completed in about half an hour. In routine operation at the foundry, the method of spectrographic analysis described has shown itself more reliable than chemical wet methods. The average accuracy of a single determination deviates from the actual amount present by not more than ±1% of the amount of the element present, and the maximum errors observed amount to less than five times the average uncertainty.

Acknowledgments

The authors wish to acknowledge their indebtedness to Professor O. S. Duffendack of this laboratory, for his active participation in the early stages of the work and his continued interest throughout the program. They are indebted to the Campbell, Wyant and Cannon Foundry Company of Muskegon, Michigan, for the financial support of the work, and especially to Mr. A. M. Sampson of that company. In addition to being responsible for the construction and successful operation of the spectrographic laboratory at the foundry, Mr. Sampson has been actively associated with the work at the university, spending some twelve months in Ann Arbor for that purpose. His numerous suggestions have contributed materially to the speed and accuracy attained.

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Rates of Diffusion in Solid Alloys

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Carnegie Institute of Technology, Pittsburgh, Pennsylvania

HARDLY a better example could be chosen to illustrate a field of research in which physicists and metallurgists must collaborate than that of diffusion in solid metals. It becomes increasingly clear that the problem involved in explaining the magnitude of the respective diffusion coefficients is one requiring the best that modern physics has to offer, and though the problem is necessarily one in the difficult field of the solid metallic state, made even more difficult by the complications of solid solution formation, the progress in the physics of the solid state is now so rapid that the problem is by no means hopeless.

The metallurgist encounters the process of diffusion at almost every turn: the process of carburization of steel, which has been practiced for more centuries than we know, is based upon the reaction of iron or steel with a carburizing gas and the penetration inward of carbon, together with other elements in a minor degree; the relatively recently developed process of nitriding is a similar process; the manufacture of bimetal strip and of veneer metals depends upon the adhesion generated by diffusion between the component metals and alloys; the various methods of producing corrosion- and heat-resisting surfaces by impregnating the surface with metallic coatings through the operation of diffusion are important—the processes of sherardizing, calorizing, chromizing, and siliconizing are well known; the manufacture of alloys such as Carboloy by the annealing of mixed powders involves diffusion; but even more important from the metallurgical point of view, the reactivity of alloys as measured by the rates of age hardening and of transformation, the rates of homogenization of castings, and the rates and types of reaction of solid metals with gases can be shown to be intimately related to rates of diffusion, and though the analysis is difficult and attended by many extraneous effects, the basic problem is one of diffusion. I have discussed these matters elsewhere in considerable detail;[13] this brief commentary should suffice for the present purpose.

It seems certain that the nature of metallurgical research should undergo some basic changes. Whereas in the past the metallurgist has necessarily been preoccupied with a purely descriptive attack upon alloy behavior, the development of the science is now such that a more meticulous attitude toward the details of the physical and chemical processes involved is both possible and necessary. We need an increasing amount of work of a purely scientific character in metallurgy, knowing well that an increasing understanding of the science of metals is the best assurance of progress in engineering metallurgy.

In order to bring this address within a reasonable compass, I shall limit myself to a discussion of the data on diffusion in binary systems, and further to diffusion within single solid solution ranges, avoiding all discussion of the generation of phase interfaces, of the effect of distortion and of impurities, of diffusion along grain boundaries and on surfaces, and of anisotropy of diffusion in noncubic systems. The data quoted are those generally available in the literature supplemented by data recently obtained in my laboratory.

It is admittedly too early to proceed very far in the evaluation of the factors which determine the magnitude of diffusion coefficients: too few diffusion coefficients have been accurately determined, for there are a great number of experimental complications, and with trustworthy diffusion coefficients available for only a relatively few binary systems it is difficult by comparison and analogy to detect the factors concerning the nature of the metallic state which may operate. What I shall have to say of the values of the diffusion coefficients in binary systems will therefore not be particularly instructive, but will at least present much matter for thought, which I take it is the purpose of a symposium such as this.

Methods

It is well known that diffusion data are treated by means of Fick's law, which is an analog of Fourier's law of heat flow. The differential equation is

$$\frac{dc}{dt}=D\frac{d^2c}{dx^2}, \qquad (1)$$

where c is concentration, t is time, x is distance from the diffusion interface, and D is the diffusion coefficient, expressed in cm²/sec. This equation assumes D to be invariant with concentration; rewriting, we have

$$\frac{dc}{dt}=\frac{d}{dx}\left(D\frac{dc}{dx}\right), \qquad (2)$$

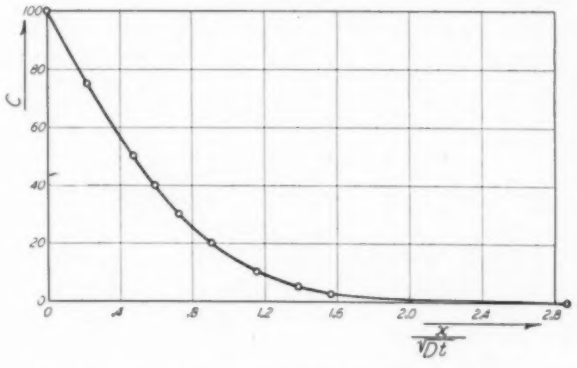


FIG. 1. Plot of theoretical diffusion-penetration curve. The abscissa is distance from the interface for unit time and unit D.

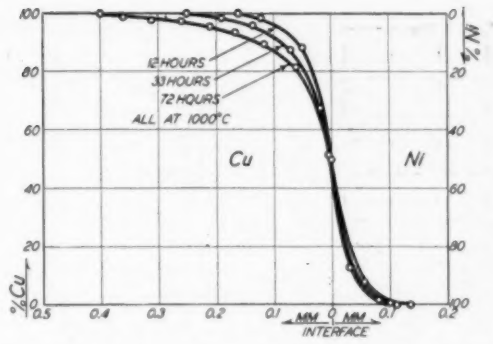


FIG. 2. Penetration curves, copper and nickel, showing compositions at different distances from the interface.

a solution for which will provide D values pertaining to particular concentration values within a concentration range. Eq. (1) may be solved readily for various boundary conditions,[13] but will furnish only approximate information on the variation of D with concentration; nearly all of the diffusion data now available have been treated in this limited way. A solution to Eq. (2) has been furnished recently by Matano[12] and should be used.

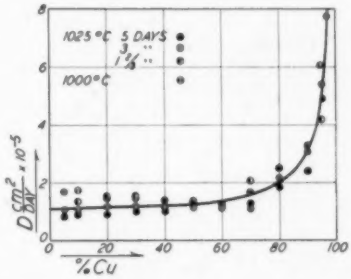


FIG. 3. Plot of diffusion coefficient as a function of concentration for the copper-nickel system.

Fig. 1 gives a plot of the solution to Eq. (1) under the condition that the initial concentration at the diffusion interface does not alter during the course of the experiment; deviations from this ideal course signify variation in D with concentration. Fig. 2 shows a series of diffusion penetration curves for the system Cu-Ni (Cu electrodeposited on a bar of Ni); it will be noted that diffusion proceeds both into the Ni and into the Cu and that the penetration is less marked in the Ni-rich alloys than in the Cu, signifying that D is lower in the Ni-rich alloys. These curves analyzed by the Matano method give the curves shown in Fig. 3. It will be seen how markedly D varies with concentration in this simple system.

It will be noted here that a single D value

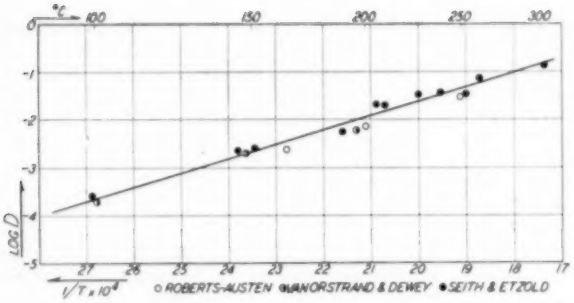


FIG. 4. Diffusion of gold into lead.

suffices for a single composition: to consider the rate of diffusion of Cu and the rate of diffusion of Ni at one composition as two individual quantities is meaningless. Brief consideration will reveal that an equal number of atoms must diffuse in either direction past a constant lattice reference point. This is the sense of the Matano solution to Eq. (2).[a]

All of the diffusion data now available show a variation with temperature of the form given in Eq. (3):

$$D = A \cdot e^{-b/T}, \tag{3}$$

where T is the absolute temperature and A and b are constants. This equation is usually written

$$D = A \cdot e^{-Q/RT} \tag{4}$$

for reasons which we shall see later. In logarithmic form, this equation becomes

$$\log_e D = \log_e A - Q/RT. \tag{5}$$

Thus, $\log_e D$ plotted against $1/T$ will give a straight line, as shown in Fig. 4 for the diffusion of Au in Pb, for which Q/R is the slope.

Ideal Cases

Owing to complications originating in grain boundaries, to which brief reference will be made later, the simplest type of diffusion, and that which might be most successfully treated in a physical way, is that which will occur between two single crystals of metals brought into intimate atomic contact at the diffusion interface. Only one case of this sort has been studied, namely, that of W and Mo, in which Mo was deposited on a single crystal of W from the vapor state, forming a continuous lattice with the W[11]. Generally it is impossible to provide such specimens, and less satisfactory and sometimes indirect methods must be used.

From the chemical standpoint, the simplest type of diffusion is that which operates in a lattice composed of one type of atom; namely, self-diffusion. Using radioactive isotopes of Pb and of Bi the self-diffusion coefficients of Pb and Bi have been measured[2–4, 7, 15, 17] and serve as comparison values for the rates of diffusion of foreign atoms. von Hevesy[6] has also approximated the rates of self-diffusion in Ag and W from the values in binary systems of Ag with Au and of W with Mo; the values of D for self-diffusion in cm²/sec. calculated at 18°C are as follows: Pb, $D = 2.5 \cdot 10^{-20}$; Ag, $D = 1.1 \cdot 10^{-24}$; W, $D = 5.0 \cdot 10^{-64}$. Thus we see that at a given temperature, the rate of self-diffusion is inversely related to the melting point, a fact of some general significance.

Complications

Measurements of the diffusion coefficient are difficult to perform. No summary of data should pass without a clear statement of the pitfalls. Indeed much of the data which must be included in a summary such as this are subject to criticism on one or more counts.

The metallurgist will readily see that the rate of diffusion at the grain boundary may well be greatly different from that within the grain, for he is acquainted with many phenomena which can be explained at least in part in this way. The types of diffusion are shown in Fig. 5, in

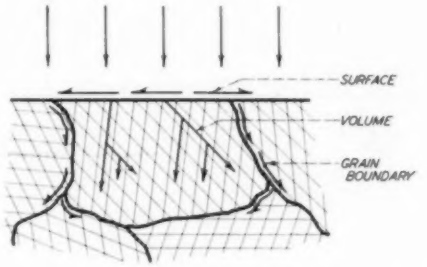
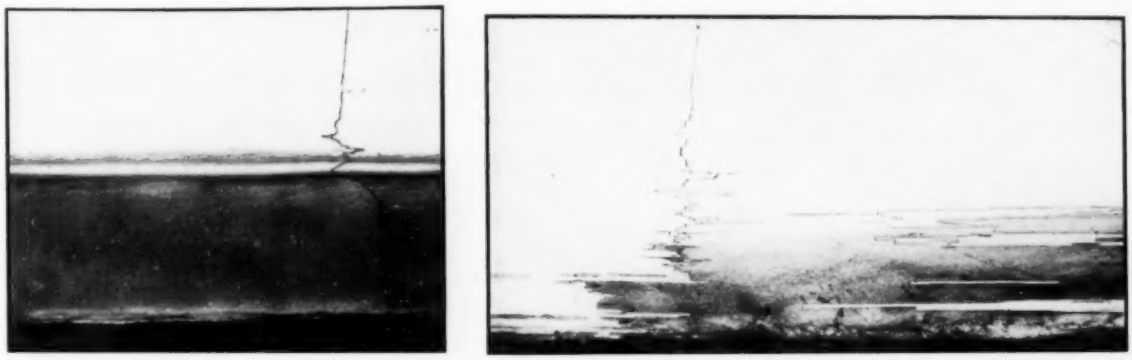


FIG. 5. Types of diffusion in crystal aggregate.

[a] Matano based his solution on equal weights of diffusing atoms on either side of the diffusion interface, whereas equal number of diffusing atoms on either side of a diffusion interface described by a lattice reference point is the correct procedure. A comparison between Matano's original method and the method modified in this way shows only an extremely slight difference between the calculated D values—a difference very much less than the experimental error of the measurements.

which anisotropy of diffusion within a single crystal of a noncubic metal is shown, and in which in addition intercrystalline and surface diffusion are also indicated.

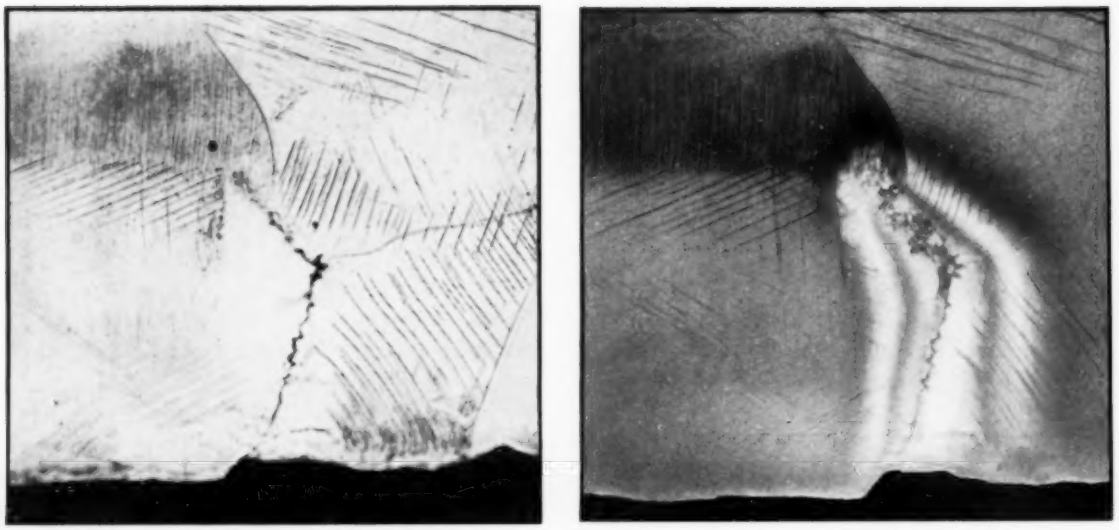
Indeed the difference between the rates of intracrystalline and intercrystalline diffusion may be very great: at 2400K. Th diffuses 100 times as rapidly at the grain boundary as within the grain;[9] similar effects have been noted in the systems Mo-W[11], Al-Cu[13], W-C[22], etc. This, of course, requires that the apparent rate of diffusion should increase as the grain-size decreases—that there should be a grain-size effect. Strangely, the effect is absent in some systems: the rate of self-diffusion in Pb does not vary with grain-size variation;[17] little or no grain-boundary effect occurs in the systems Fe-C, Fe-N, and Fe-H.[13] In the large majority of cases reported in the literature the effect has been ignored completely, and the critic is at a loss to know how to regard the data. In some cases the presence or absence of a grain boundary effect is determined by the method of performing the diffusion process; Fig. 6 shows the microstructure of a bicrystal of Cu which has absorbed Zn from the vapor state—the staining effect shown in the left-hand photograph, occurring at a definite Zn concentration, crosses the grain-boundary without change in direction where a more rapid rate of diffusion would be shown by an inward penetration of the stain. The microstructure on the right in Fig. 6, shows a similar sample which has been etched differently, and we note that the metal has been recrystallized; evidently, then, we must consider grain-size changes accompanying and caused by the process of diffusion as an additional complication. On the other hand, when Zn is lost from a bicrystal of α brass, the Zn leaves the grain boundary more rapidly than the grain, as shown by Fig. 7. This effect evidently originates in the contraction in volume accompanying the loss of Zn and the resultant opening of the specimen along the grain boundary. It seems reasonable, then, to assume that there is no *true* grain-boundary effect in α brass, but how far this might be extended to include all Cu and similar alloys is quite uncertain.



a b

FIG. 6. Penetration of zinc into bicrystal of copper. Left: Bicrystal of Cu packed in α brass chips; held one week at 775°. Etching: Ammonia+hydrogen peroxide. ×100. Showing α brass at bottom (stained), Cu at top, grain boundary running from top to bottom, and no preferential penetration along grain boundary. Right: Same treatment as left side. Etching same as left, except that there was little staining. Showing recrystallization along grain boundary.

In addition, the possible effects of impurities must be carefully considered, for data are available which show that very small quantities of impurities may alter the diffusion coefficient several fold.[13] Furthermore, it is necessary to provide a contact between two diffusing bodies so intimate that atom transport may occur as readily as within a true solid. Usually, electrodeposition is employed, but the possible role of intervening oxide films as diffusion barriers has seldom been considered. A different sort of difficulty arises when measurements are desired on a system when the degree of solid solubility is not high, for in such cases it is difficult to find an analytical method which will be accurate enough to establish a concentration depth curve.[13] In every case, then, the experimenter must exercise a great deal of ingenuity in



a b

FIG. 7. Loss of zinc from α brass bicrystal. Left: Bicrystal of α brass (70:30) held one hour at 790° in vacuum. Etching: Ammonia + hydrogen peroxide. ×100; reduced 1/3 in reproduction. Showing crack along grain boundary. Right: Same treatment as left, but stained by etching. Showing loss of Zn around crack (Cu-rich portion less stained).

assembling his experiment and must be ever watchful for the operation of complicating factors. In view of this it is perhaps not strange that so few trustworthy data are available.

Physics

There seems to be little point in devising complicated atomic mechanisms for explaining the transport of atoms in the solid state, at least for the data to be presented here. Although lattice imperfections and mosaics have frequently been identified as major elements in diffusion phenomena, and though the "dissociation" of diffusing atoms in interstitial space has been postulated, there is little real justification for these complications; some experimental data are decidedly of contrary import. The process can probably be regarded as a simple one, involving the interchange of atoms on lattice positions with more justification than in any other way and certainly with more satisfaction.[13]

The type of equation representing the effect of temperature upon D, Eq. (3), immediately suggests that diffusion is a process subject to activation energies. If we take the probability of reactive collision in a chemical reaction as proportional to $e^{-E/kT}$ or for gram-atoms $e^{-Q/RT}$, we may then identify the Q value in Eq. (4) as the minimum energy which must be exceeded before an atom can surmount its potential barrier and become mobile, i.e., diffuse. Following this reasoning, Dushman and Langmuir[1] proposed a semiempirical diffusion expression, given in Eq. (6):

$$D = (Q/Nh) \cdot \delta^2 \cdot e^{-Q/RT}, \qquad (6)$$

where all quantities have their usual significance —δ is the interatomic distance. Whatever the theoretical justification for this equation, and whatever limitation it may suffer in application to the analogous field of the conductivity of solid salts, it does represent the data on diffusion in solid metals with surprising authenticity, as shown in Table I,[b] even when, as in the case of the system Fe-C and Fe-N, the solid solutions are interstitial rather than substitutional. These two cases are of special interest: in substitutional solid solutions the atoms of the solute occupy normal lattice points and the jump is simply from one lattice position to one of the nearest lattice positions, whereas in interstitial solid solutions the atoms of the solute lie in the interstices of the normal lattice; the success of the Dushman-Langmuir equation for these two cases thus requires that the jump of the interstitial solute atoms be from one interstice to one of the nearest interstices which is removed from

[b] The sources of these data are given in reference 13.

it by a distance equal to the nearest approach of atoms on the solvent lattice. The usefulness of this equation is great: if D is known at one temperature, it can be calculated at any other temperature (δ can be found in tables); if D and Q are known, δ can be calculated. Thus metallurgical processes which depend for their rate upon the rate of diffusion can be handled without recourse to the measurement of D: if the rate is known at one temperature, the rate at other temperatures can be calculated. In processes like rate of carburization, of homogenization, of age hardening, this equation should prove very useful.

Van Liempt[10, 11] correlated the Q value with the Lindemann theory of melting and derived the expression:

$$D = (8/3\pi) \cdot \nu \cdot \delta^2 \cdot e^{-3b^2 T_s/T}, \qquad (7)$$

where ν is the Einstein monochromatic frequency, T_s the melting point, and b a constant, usually near 2. Although the use of the Einstein ν may seem an over-simplification in view of the Debye distribution of frequencies and limiting maximum frequency and in view of the several maxima in frequency distribution curves demanded by Blackman,[14] it is possible that this simplification is not a serious one in the temperature ranges where the rate of diffusion can be measured, which are invariably high. The van Liempt equation does include an expression for melting point, which we have seen to be important in the case of self-diffusion and which we shall later see to be of some importance in binary systems. Similar equations have been proposed by others but offer no new ideas. It seems that the van Liempt equation could well be developed, but the subject is difficult, for in binary systems so many factors operate—factors relating to atom polarization, relative state of ionization, lattice distortion, and free energy variations—that a strict treatment seems difficult and probably impossible at the moment.

TABLE I. *Applicability of Dushman-Langmuir equation to diffusion data.*

SOLVENT	SOLUTE	Q	
		FROM DIFFUSION-TEMPERATURE CURVE	FROM DUSHMAN-LANGMUIR EQUATION
Cu	Zn (9.58%)	41,700	41,000
	Zn (29.08%)	41,700	38,000
	Sn (10%)	40,200	40,000
Pb	Pb (self-diffusion)	27,900	24,400
	Sn	24,000	23,200
	Tl	21,000	22,380
	Bi	18,600	21,900
	Cd	18,000	19,970
	Ag	15,200	15,700
	Au	13,000	13,300
Ag	Au	57,600	57,000
W	Th (small W grains)	94,000	96,700
	Th (large W grains)	94,450	118,200
	U	100,000	100,500
	Ce	83,000	82,700
	Zr	78,000	77,400
	Yt	68,000	70,100
γ-Fe	N	34,600	38,100
	C	36,000	36,700

Diffusion Data

In presenting the data on diffusion, the systems will be grouped with regard to the classification employed extensively in similar studies (Fig. 8) relating to other properties: (1) The systems Cu, Ag, Au, and the members of the VIII group in the periodic table; these are the systems for which in large part the atom size factors for solid solution formation are favorable and in which electrovalency effects are subordinate; they form simple solid solution systems with intermediate phases only of the superstructure type; (2) the systems of Cu, Ag and Au with metals of the B subgroups; in these favorable atom size factors are not adequate to provide extensive solid solutions because of electrovalency effects associated with the filling of Brillouin zones, leading to many intermediate phases; and (3) systems in which the solvent metal is of the class II type, in which more pronounced valency effects obtain. The third class will be considered first however, since most of the ideas now current arose from a consideration of this class.

Arguments on the factors which control the rates of diffusion in binary systems have centered chiefly around the effect of four factors, namely, atom size, melting points, degrees of solid solubility, and the relative positions of the respective components in the periodic table—in order to appraise the action of electrovalency effects. In each of the groups of alloys discussed in the following, the role of each of these factors will be discussed critically.

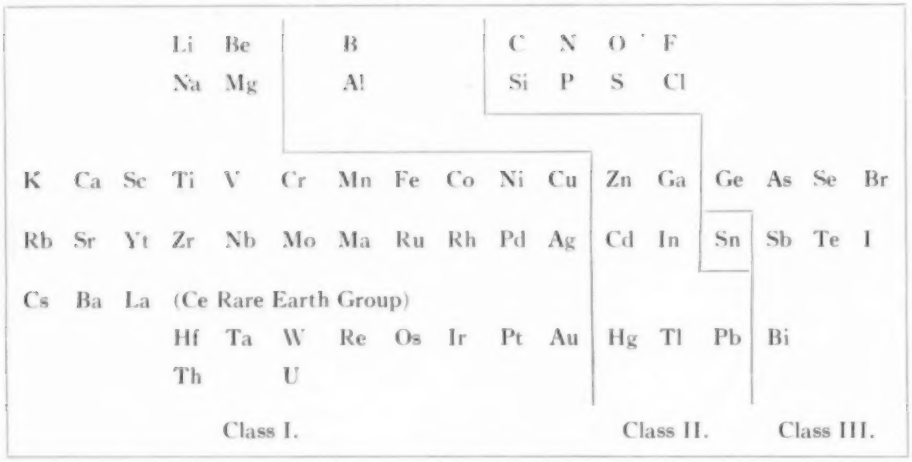

Li Be B C N O F
Na Mg Al Si P S Cl
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br
Rb Sr Yt Zr Nb Mo Ma Ru Rh Pd Ag Cd In Sn Sb Te I
Cs Ba La (Ce Rare Earth Group)
Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi
Th U
Class I.
Class II.
Class III.

FIG. 8. Periodic Table.

Alloys of Lead

Fairly complete data on diffusion in lead alloys have been furnished by von Hevesy and Seith;[5, 6, 16, 18, 19] these are plotted in Fig. 9 and summarized in Table II. In reviewing these data it must be remembered that they represent limiting diffusion rates: the diffusion is that which obtains between an alloy with a few percent of the alloying element and pure lead; accordingly, no information is afforded concerning the variation of D with concentration.

It will be noted immediately that the rate of diffusion is slowest in self-diffusion and increases toward the left of the table, that is, as the alloying elements differ chemically—as judged from their positions in the periodic table—in increasing degrees from Pb, and that concomitantly the heat of diffusion decreases. We may readily suppose that at constant temperature a high Q value should imply a low diffusion velocity, i.e., a smaller number of atoms with the requisite energies of activation. Together with this effect we note that with increasing diffusion velocity toward the left there are decreasing degrees of solid solubility, decreasing (Goldschmidt) atomic radii, and increasing melting point, though this behavior is not quite regular.

We may presume that the symmetry of the charge distribution in a crystal will be only slightly disturbed if an atom is replaced by one quite similar chemically, and that such an atom might possess a mobility quite similar to that of the parent atom; such is the case for Sn in Table II. As, however, the replacing atom differs chemically more greatly from the host atom, special effects will enter: electrovalency effects will appear, with resultant atom polarization and a dissymmetry of the charge distribution; the atom will now, in a wholly or partly ionized state, possess a size which may be quite different from the Goldschmidt value in the pure state. (The ion Mg^{++}, for instance, has a radius of 0.78A, whereas the radius of the unionized atom in the Mg crystal is 1.60A.)[8] These effects should be mutual, affecting both atoms, and they may be presumed to increase as the chemical difference increases. The exact state of distortion of the lattice and the charge distribution in solid solutions is a wholly unsolved problem; when speaking of distortion in solid solutions, it is

TABLE II. *Diffusion of metals in lead.*

METAL	Au	Ag	Cd	Bi	β–Tl	β–Sn	Pb SELF-DIFFUSION
D, cm²/sec., at 285°C	$4.6 \cdot 10^{-6}$	$9.1 \cdot 10^{-8}$	$2 \cdot 10^{-9}$	$4.4 \cdot 10^{-10}$	$3.1 \cdot 10^{-10}$	$1.6 \cdot 10^{-10}$	$7 \cdot 10^{-11}$
Q	13,000	15,200	18,000	18,600	21,000	24,000	28,000
Crystal system of solute	f.c.c.	f.c.c.	c.p.h.	rhomb.	f.c.c.	tetr.	f.c.c.
Maximum solid solubility, atomic percent	0.05	0.12	17	35	79	29	100
Atomic radii (Goldschmidt), A	1.44	1.44	1.52	1.82	1.71	1.58	1.74
Melting points, °C	1063	960	321	271	303	232	327

TABLE III. *Diffusion of metals in copper.* (All compositions in atomic percent.)

METAL	Zn (FROM BASE 13.6% ALLOY)			Zn (FROM BASE 29.6% ALLOY)			Al (FROM BASE 17.8% ALLOY)			Si (FROM BASE 10.85% ALLOY)			Sn (FROM BASE 5.6% ALLOY)		
COMPOSITION	0% Zn	4% Zn	10% Zn	0% Zn	4% Zn	27% Zn	0% Al	4% Al	16% Al	0% Si	4% Si	8% Si	0% Sn	4% Sn	5% Sn
D, 10^{-10} cm²/sec., at 750°C	1.4	1.5	3.2	3.1	3.6	56.0	1.6	1.7	10.8	2.0	2.8	8.6	2.1	22.2	33.5
Q	—	34,100	—	—	31,400	—	—	40,400	—	—	64,200	—	—	54,000	—
Crystal system of solute	c.p.h.	—	—	c.p.h.	—	—	f.c.c.	—	—	diam.c	—	—	tetrag.	—	—
Solid solubility at peritectic temp.	32	—	—	32	—	—	16	—	—	11	—	—	7.5	—	—
Atomic radii (Goldschmidt), A	1.374	—	—	1.374	—	—	1.40	—	—	—	—	—	1.582	—	—
Melting points of solute, °C	419.4	—	—	419.4	—	—	660	—	—	1420	—	—	231.9	—	—

customary to designate only the deviation of the average interatomic distance from that of the pure solvent and wholly to disregard the highly localized type of distortion resulting in warped atom planes and dissymmetry in charge distribution. Chiefly then to polarization, to electrovalency effects, must this effect of chemical difference be ascribed. It is no great surprise that as such disturbances increase, the solid solubility decreases. Although the true size of the atom in solid solution cannot be known accurately, it is interesting to see that decreasing size accompanies increasing mobility in the Pb system, suggesting that the smaller the atom the more readily it can diffuse through a lattice composed of atoms of a given size. The same relationship obtains in alloys of Au (Table V); the relationship, however, is not consistent, for we note in the Pb series that Bi which has a larger atomic radius than Pb diffuses more rapidly than Sn which has a smaller, and we shall see that the relationship is not followed in alloys of Ag (Table IV). Evidently we must conclude that

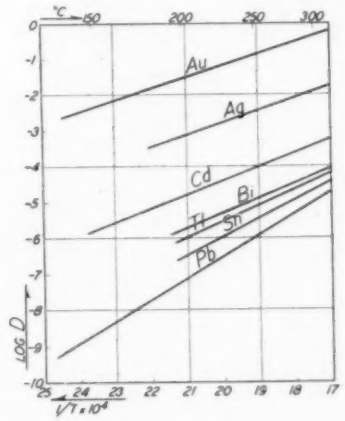


FIG. 9. Diffusion of various metals into lead.

atom size as represented by the radius for a coordination number of 12 (the Goldschmidt radius) is of inferior and uncertain effect upon the rate of diffusion, and that chemical effects play a predominant role.

The effect of melting point is in a different category. It has been shown that the rate of self-diffusion at a constant temperature decreases as the melting point increases—that the rate of self-diffusion and melting point are inversely related. We now note that the rate of diffusion in lead increases as the melting point of the solute atom increases. Let us consider, in connection with the values of D for Au in Pb, similar values for Pb in Au: at 150° the value of D for Au in Pb is $4.6 \cdot 10^{-8}$ cm²/sec., whereas at 141° the value of D for Pb in Au is $3.5 \cdot 10^{-16}$ cm²/sec.[5] Here also we may see that the rate of diffusion is inversely related to the melting point. In this connection it may be noted that the Au atom is small and retains its valence electron strongly, and that the Pb atom is large and susceptible to deformation which gives the Au atom a rather considerable mobility, judging from comparable work on the electrolytic conductivity of solid salts, whereas the Pb atom is nearly immobile.[5]

In further comment on the effect of temperature on the rate of diffusion it should be noted that Bi when added to Pb lowers the melting point of Pb and that in this alloy the rate of self-diffusion of Pb at a constant temperature is increased, whereas Tl, which when added to Pb increases the melting point, is without effect on the rate of self-diffusion.[18] The case of Cd-Pb, however, is somewhat anomalous, for despite the near equality in the melting points, a considerable difference in the D values for Cd in Pb and Pb in Cd obtain. In this case the differing crystal

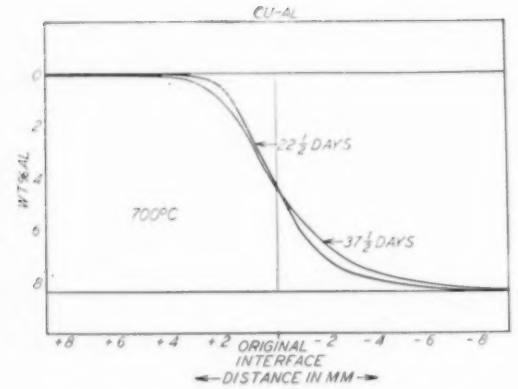


FIG. 10. Diffusion-penetration curve for a Cu-Al alloy with 8.4 weight percent Al diffusing into pure Cu.

structures of the two metals and the resulting differences in lattice dynamics may be the determining factor and simple melting point differences unimportant.

Further than this, little can be said. The series of alloys studied is one of the more difficult ones to attack from the view point of modern theories of alloy structure and an exact analysis of the factors involved seems rather remote.

Alloys of Copper

Since so much success has been attained in the study of the factors which determine limits of solid solubility and the concentration ranges of intermediate phase and the crystal structure of these phases in the systems of Cu, Ag and Au with the metals of the *B* subgroup by Westgren,[21] Hume-Rothery,[8] and Jones,[14] it seemed reasonable to believe that a study of diffusion rates in these systems might lead to a similar success in understanding the factors which determine the value of *D*. For this reason the rates of diffusion in a series of Cu alloys have been studied in detail in my laboratory during the past three years; this series included the systems Cu-Zn (two base compositions), Cu-Al, Cu-Si, Cu-Sn, Cu-Cd, Cu-Be, Cu-Ni_2Si, for which preliminary results on the first four are reported here.[c]

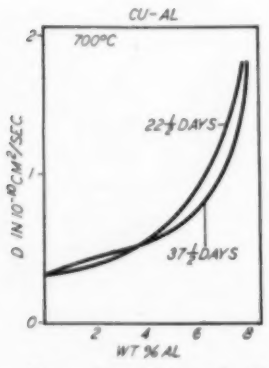


FIG. 11. Plot of *D* *versus* concentration for the α solid solution of Al in Cu.

Two diffusion-penetration curves are shown in Fig. 10 for an alloy with 17.8 atomic percent Al (8.4 weight percent) at 700° for 22½ and 37½ days, respectively, diffusing into pure (electroplated) copper. From curves of this sort the values of *D* at any composition can be calculated, as shown in Fig. 11. We note that *D* increases sixfold up to the highest Al concentration. This is a surprising result, and to the metallurgist it must be pointed out that this fact, if generally true for alloy systems, is of great importance in considering the rate of reaction in age-hardening systems. Since the initial precipitation from an age-hardening alloy occurs from a solid solution of the concentration given by the alloy composition, the initial rate of precipitation is thus controlled by the rate of diffusion at this composition; but as precipitation proceeds the matrix alloy becomes depleted in solute and thus the subsequent rates of precipitation are controlled by the rates of diffusion at these new less concentrated matrix compositions. This would signify, then, that the initial rate of precipitation should be more rapid than the rates later in the process.

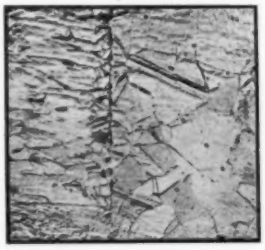


FIG. 12. Microstructure of diffusion specimen. Cu at left, Cu-Cd alloy at right. Showing columnar grains in Cu plate, and showing interface. Etch: nitric acid; 300 diameters.

Fig. 12 shows the microstructure of the electroplated Cu-Cd alloy and illustrates the grain-structure in the alloy and in the Cu, and shows also the diffusion interface, marked by deep etching. As diffusion proceeds the Cu electroplate recrystallizes, becoming polyhedral, and distortion effects become evident in the profuseness of twin bands. This is shown in Fig. 13, which shows Cu at the top and a Cu-Si alloy at the bottom. The concentration differ-

[c] This work has been done by Dr. F. N. Rhines of this laboratory; the full details will be published later.

TABLE IV. *Diffusion of metals in silver.* Ag-atomic radius = 2.883; m.p. = 960.5°C.

METAL	Sb	Sn	In	Cd	Au	Pd
D, cm²/sec., at 760°C	$1.4 \cdot 10^{-9}$	$2.3 \cdot 10^{-9}$	$1.2 \cdot 10^{-9}$	$9.5 \cdot 10^{-10}$	$3.6 \cdot 10^{-10}$	$2.4 \cdot 10^{-10}$
Q	21,700	21,400	24,400	22,350	26,600	20,200
Crystal system of solute	rhomb.	tetrag.	f.c. tetrag.	c.p.h.	f.c.c.	f.c.c.
Max. solid solubility in atomic percent	5	12	19	42	100	100
Atomic radius (Goldschmidt), Å	1.614	1.582	1.569	1.521	1.438	1.372
Melting point, °C	630	231.9	155	320.9	1063	1555

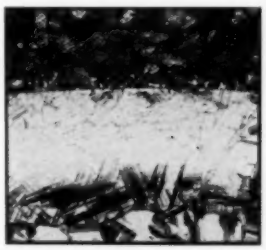


FIG. 13. Microstructure of diffusion specimen. Cu at top, Cu-Si alloy at bottom. Following diffusion. Showing polyhedral structure in Cu and twinned structure in alloy. Etch: nitric acid; 175 diameters.

ences in diffusion zones prevent uniform etching. This twinned structure is unusually complicated, as shown in Fig. 14, which is taken at a magnification of 600.

The logarithms of the diffusion coefficients obtained in this work plotted against the reciprocal of the absolute temperatures give straight lines as expected, as shown in Fig. 15, which also gives the Q value as derived from the slope.

Of particular interest is the plot of the Q values pertaining to different concentrations. This is shown in Fig. 16, the first plot of this kind that has been published for any system. The rapidly changing Q values show how greatly the energetics of the lattice change with solid solution formation. This type of curve can be transformed into a straight line if the Q values are plotted against the square of the atomic percent, as shown in Fig. 17, though what meaning this may have cannot be said.

The values obtained for the various alloys are given in Table III. It is a striking fact that the values of D extrapolated to 100 percent Cu are all nearly equal: this is not true for the Pb alloys discussed previously, nor the Ag alloys mentioned below. The rate of increase of D with concentration increases very markedly from system to system; it is small for the system Cu-Si and large for the system Cu-Zn. Roughly, the rates of diffusion at a constant composition, 4 percent, vary with the distance of removal of the elements in the periodic table, and again it seems clear that electrovalency effects, atom polarization and distortion are of major importance. The rates of diffusion increase with increasing size of the diffusing atom, which is

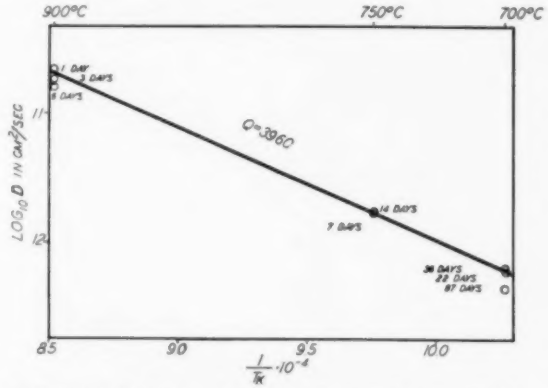


FIG. 15. Diffusion data for a 6 atomic percent Al, Cu-Al alloy.

contrary to the behavior of the Pb alloys. And strangely, the Q values do not decrease as the D values increase. There is little or no relationship with the melting points of the solute.

Thus, though the maximum solid solubility in these systems appears at concentrations where the number of valency electrons per atom is approximately 1.4 by reason of the filling of the Brillouin zones,[8, 14] the rate of diffusion at maximum concentration seems to bear no relation to the valency electron concentration, for the D values are widely different at maximum

FIG. 14. Same as Fig. 12, showing details of twinned structure. Etch: nitric acid; 600 diameters.

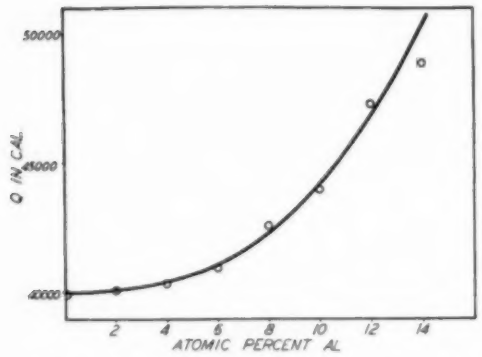


FIG. 16. *Q versus* concentration for a 4 atomic percent Al, Cu-Al alloy.

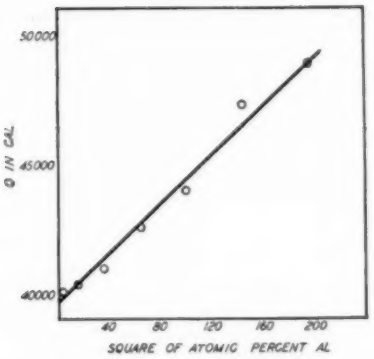


FIG. 17. *Q versus* concentration for a 4 atomic percent Al, Cu-Al alloy, with concentration plotted as the square of the atomic percentage.

concentration; nor do the D values at maximum concentration vary consistently with the degree of solid solubility. There is, of course, little reason to think that the D values should bear a simple relationship to the valency electron concentration, for there is no obvious relation between a valency structural effect, as represented by Brillouin zones, and the binding forces which determine the mobility of an atom in a lattice. Thus, a given atom might fill the first Brillouin zone for both Cu and Ag at the same valency electron concentration, but it does not follow that the lattice binding forces are then equal any more than it follows that they are equal in Cu and Ag. The free energy of a solid solution field at the limit of solid solubility merely becomes equal to the free energy of the intermediate phase with which it is in equilibrium, but these equilibrium free energies need not be the same in different systems. Unfortunately it is not yet possible to calculate the energies of atoms in solid solution from which the maximum solid solubility could be calculated.

Alloys of Silver

Seith and Peretti[20] recently studied the rates of diffusion of a number of metals in silver, employing in each case base alloys with only two atomic percent of the alloying element. Their data are given in Table IV, in which the rate of diffusion of Au may be taken as near the rate of self-diffusion in Ag. Obviously no data were obtained on the variation of either D or Q with concentration. Thus, contrary to the data on Pb alloys, the rates of diffusion increase with increasing atom size (to the left of Au): the rates of diffusion increase with increasing melting point of the solute, though Pd seems exceptionally low from this point of view. There is some relation to degree of solid solubility, D increasing with decreasing solid solubility as in Pb alloys, but Sb is exceptional. These data again indicate the importance of relative position in the periodic table, but beyond that they furnish little general information.

Alloys of Ag and Au with Cu, Pd, Pt, Ni

Fig. 18 is a plot of the diffusion data at 900°C for the systems Au-Ni, Au-Pd, Au-Pt[11]. Several striking things emerge from this plot. It will be noted that the diffusion coefficients for Au in the elements Ni, Pd and Pt are all equal, but that the diffusion coefficients for these three elements in Au vary widely. This seems inexplicable where the opposite case might have been not unsurprising. It will, however, be noted that the rate of diffusion is the more rapid in the lower melting alloys—those rich in Au. This seems to be one valid generalization in isomorphous systems; it is illustrated also for the Cu-Ni system in Fig. 3. Judging from the data

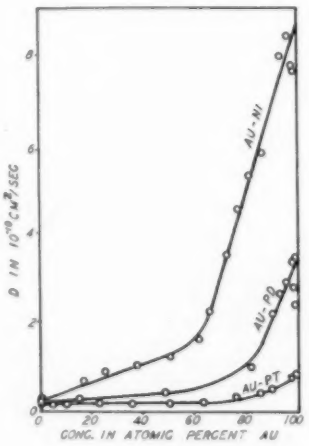


FIG. 18. Diffusion coefficients at 900°C *versus* composition for the systems Au-Ni, Au-Pd, Au-Pt.

TABLE V. *Diffusion in noble metals.*

Solvent metal Ag at. radius = 1.442; m.p. = 960.5; Au at. radius = 1.438; m.p. = 1063.

SOLUTE METAL	Au	Ag-Au ALLOY	Pd	Ag-Pd ALLOY, 20% Pd	Cu	Au-Cu ALLOY, 10% Cu	Ni	Pd	Au-Pd ALLOY	Pt	Au-Pt ALLOY
D, cm²/sec. at 900°C	$1.6 \cdot 10^{-9}$	$1.6 \cdot 10^{-8}$		$1.1 \cdot 10^{-9}$	$9.0 \cdot 10^{-9}$	$5.0 \cdot 10^{-9}$	$0.34 \cdot 10^{-10}$ Ni rich $6.0 \cdot 10^{-10}$ Au rich	$0.22 \cdot 10^{-10}$ Pd rich $2.3 \cdot 10^{-10}$ Au rich	$1.0 \cdot 10^{-10}$	$0.14 \cdot 10^{-10}$ Pt rich $0.61 \cdot 10^{-10}$ Au rich	$0.77 \cdot 10^{-10}$
Q	29,800	26,600		20,200	27,400	—	—	—	37,400	—	39,000
Atomic radius (Goldschmidt), A	1.438	—	1.372	—	1.276	—	1.244	1.372	—	1.385	—
Melting point, °C	1063	—	1555	—	1083	—	1452	1555	—	1755	—

on Pb alloys we might expect the highest metal to show the most rapid diffusion rate in Au, but the contrary is the case: the rates of diffusion are in inverse order of the melting points.

This lack of correlation between the melting points and the rates of diffusion is evident in the data in Fig. 5.[d] The Q values show normal behavior, for the higher D values are accompanied by lower diffusion rates; the larger atoms diffuse the more slowly.

It is remarkable that the diffusion coefficients in the Cu-Ni system, shown in Fig. 3, vary so greatly with composition. This is nearly solid solution system—the liquidus and solidus temperatures vary regularly from one component to another, the elements are quite similar chemically (though they vary electronically), and the atomic volumes are nearly equal; the wide departure of the diffusion coefficients from rule of mixtures values is probably to be ascribed to the difference in electronic structures of the two components. It is also noteworthy that the diffusion coefficient changes little between zero and 70 percent Cu; the maximum departure from the rule of mixtures values does not appear at 50 atomic percent as might be expected.

It is not easy to summarize these data. Apart from the evident role played by the chemical or electrovalent factor, little by way of generalization appears. With the very great importance of the diffusion process in metallurgical phenomena, the metallurgist will doubtless profit by any attention given by the theoretical physicist to this problem.

[d] The sources of these data are given in reference 13.

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Modern Theory of Solids. II

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In the preceding article we reviewed the classical theories of the solid state, and sketched an outline of the modern wave mechanical theory. We saw that the valence electrons of a solid occupy an energy spectrum composed of zones of energy levels, and that the observed differences among various solids can be correlated largely with differences in the distribution and population of these zones. In this issue we shall first discuss in turn each of the five main types of solids, to see what explanation the zone theory offers for their distinguishing peculiarities. Following this, we shall review very briefly the progress of the theory in interpreting certain structure-insensitive volume properties.

IV. The Five Solid Types

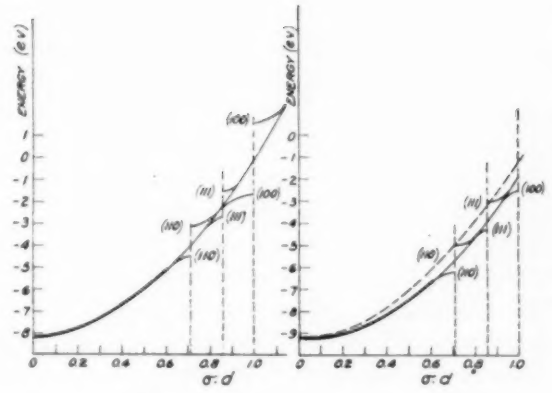
(*1*) *Pure Metals*[1]

THE alkali metals have been treated quantitatively and the accuracy of the resulting zone spectra has been checked by direct computation of the heats of sublimation. The energy *versus* wave number curves for Na and Li are shown in Fig. 15, and the spatial electronic distribution in Fig. 16. These crystals are body-centered, but the results would be very much the same if they were face-centered. In both substances, the discontinuities in the $E(\sigma)$ curves are very small, and there is considerable overlapping of zones. The charge distribution, correspondingly, is quite flat throughout most of the lattice, so these substances will fit into the Sommerfeld picture very closely: the motion of the electrons is not greatly influenced by the periodicity of the lattice potential field. Fig. 17 shows symbolically how the zones arise from the atomic energy levels and how they overlap as the atomic spacing is decreased. This behavior is characteristic of all the monovalent metals, including the noble metals Cu, Ag and Au.[2]

The behavior should not change fundamentally as one goes to the elements of the second column. The energy states in the isolated atoms are more widely separated, particularly in the lighter elements, so that overlapping of zones cannot be expected to quite the same degree. Passing to the third column, we find from experiment that B is a semiconductor, and infer that at the equilibrium spacing either the zones have not overlapped, or else that after overlapping they have again separated. A study of diamond, to be described later, shows that the latter is more probable: we shall return to this point. The crystal structure of B has not been determined, but we can predict that each unit cell will contain an even number of atoms, since each atom has three valence electrons and the solid lacks the metallic properties which inevitably go with half-filled zones. Al has one atom, and thus an odd number of valence electrons, in the unit cell—it is therefore a metal regardless of how the zones overlap. Actually, we may expect a zone behavior similar to that of B.

The light elements of the remaining columns are not metals, and we shall discuss their peculiarities later. The heavy elements in these columns, on the other hand, are practically all metals. This is reasonable, for we recall that the atomic energy states in these heavier elements are dense, so that in the formation of the lattice overlapping of zones is almost unavoidable.

A prediction about the binding energy is also possible. The overlapping of close-lying levels makes the density of electronic states higher in the solids of these heavy elements than in the monovalent and divalent metals. Many low energy states are therefore available for the valence electrons to occupy, without violating the exclusion principle. Fig. 18 shows the typical



Na Li

FIG. 15. $E(\sigma)$ curves for Na and Li, showing the first set of discontinuities in three lattice directions. The abscissae are $\sigma.d$, where d is the lattice constant (cube edge, 4.23A for Na and 3.46A for Li). The Na curves follow the free-electron parabola more closely than do those for Li. The heavy lower section shows the extent to which the levels are filled. Energy is in electron volts, with the zero of potential outside the metal.

behavior of bands in any one of the long periods. The nd band overlaps the $(n+1)s$ and $(n+1)p$ bands. These s, p, and d bands contain, respectively, one, three, and five zones. If the atomic p level is low lying we may expect roughly half of the levels of the nine zones to lie below the atomic s and d levels, but if the p level is high there may be less. If the p level is very high, the minimum number of depressed zones will be about three, that is, half of the six s and d zones. As long as the electrons fill depressed zones we may expect the binding to increase, but when levels which are higher than the mean of the

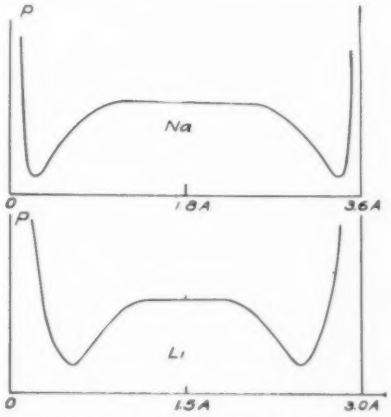


FIG. 16. Relative scale plots of the charge distribution of valence electrons between neighboring atoms, in Na and in Li. The flatness of the curves about the midpoints indicates a distribution nearly uniform throughout the unit cell.

atomic s and d states are filled, we may expect the binding to decrease. That is, we would expect the binding energy of the metals in one of the long periods to increase with atomic number at first, reach a maximum for atoms containing between six and nine valence electrons and then decrease again. This fits the observations: the element with highest cohesive energy in the first long period is Fe which has eight valence electrons, while that in the third is W with six. The data for the second period are not complete.

(2) *Ionic Crystals*[3]

Both zone structure and cohesion have been quantitatively investigated for the simplest monovalent halides. It is most convenient to consider the zones as arising from the electronic energy levels of the isolated *ions*, rather than the

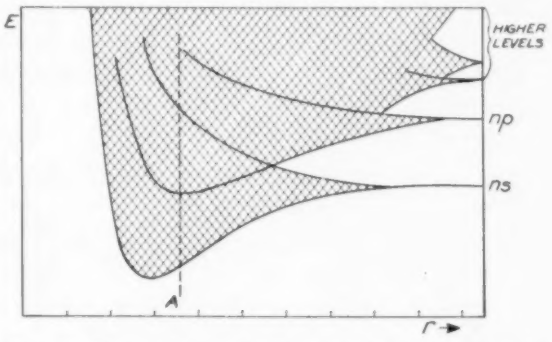


FIG. 17. Shows schematically the behavior of the atomic energy levels as an alkali metal lattice is contracted. At the equilibrium distance A the spectrum is "continuous" above the lowest curve.

atoms. Calling the positive ion I^+ and the negative ion I^-, the behavior of the lowest s and p valence levels, as the ions are brought together to form a lattice, is shown symbolically in Fig. 19. The electronic levels of the positive ion are sent upward as the field of the neighboring negative ions becomes effective, while those of the negative ion are sent downward because of the field of neighboring positive ions. The result is a low lying s band, s_I, arising from the s level of the negative ion, and a higher one, s_{II}, arising from the s level of the positive ion. Between these two, arising from the p level of the negative ion, is a p band, p_I. s_{II} and p_{II} presumably overlap with bands arising from higher ionic levels to form a continuum for high energies. s_I and p_I

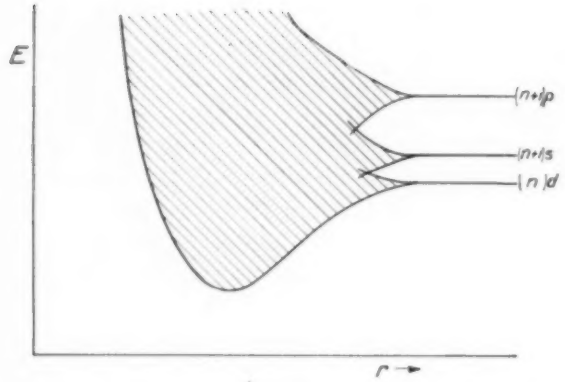


FIG. 18. Shows schematically the lowest band, containing nine zones, for a solid formed by any element in one of the long periods. The binding energy depends on the extent to which the band is filled, and has a maximum when it is filled approximately to the height of the atomic s and d levels.

contain one and three zones, respectively, which are just filled by the eight valence electrons in the unit cell.

$E(\sigma)$ plots for LiF at the observed lattice distance are shown in Fig. 20, along with the charge distribution. Here, s_I and p_I have not yet crossed at the equilibrium distance, which corresponds to $r=A$ in Fig. 19. It will be noted that most of the valence electronic charge is near the negative ion. This behavior is typical for all the monovalent halides. In other words, the quantum calculations lead to approximately the same average charge distribution as was assumed in the Madelung-Born theory. The deviation between the classical and quantum pictures is tied up with the width of the energy bands, since this measures the extent to which the cohesion is like that in metals (and in valence crystals, as we shall see). This width would be zero in the classical picture. The binding energy, computed on the zone theory, contains other terms, connected with this band width, in addition to the ionic terms which alone were treated by Madelung, Born, etc. These additional terms largely cancel one another, and this convenient canceling probably explains the success of the classical calculations.

There have been no detailed computations, using the modern picture, for divalent ionic crystals of the type MgO. The results of Born for the binding energy of these crystals often deviated badly from the experimental observations. We infer that the terms connected with band-width, which the classical theory does not include, and which practically cancel one another in the alkali halides, are not so nicely balanced in these divalent solids. The equilibrium lattice spacing probably corresponds to the distance B in Fig. 19, where the s_I and p_I bands have overlapped. The crystals are nonconductors, of course, since both bands are filled, but the width of the combined band is large, and the cohesion is therefore to some extent like that of a metal or a valence crystal. The electronic charge is still unequally distributed, with more of it around the O than around the Mg. The crystals thus have ionic properties, such as ionic conductivity at high temperatures.

(3) *Valence Crystals*

A semiquantitative treatment of the electronic states has been carried through for diamond.[4] The atomic configuration is $2s^22p^2$, which means

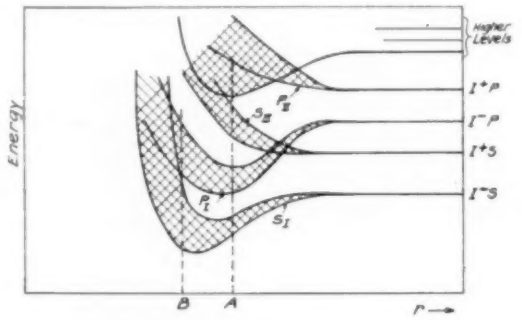


FIG. 19. Representative behavior of the ionic energy levels as an ionic crystal is contracted toward the equilibrium spacing.

that there are four valence electrons per atom and eight per unit cell. The atomic $2s$ level gives rise to two zones in the energy spectrum of the solid, and the $2p$ level gives rise to six zones, making a total of eight low lying zones. Fig. 21 shows how these vary with spacing between nearest neighbors. At large spacing the two $2s$ zones form a band which is separated from the $2p$ band containing six zones. As the atoms are brought closer together these two bands intermingle, and at close spacing the eight zones are separated into two groups of four, one group going up and the other going down. This differs from the crossing in the monovalent halides inasmuch as the s and p

bands there remained relatively distinct. Evidently, the most stable state of the entire system will occur when the lowest band of four zones is occupied and the distance between nearest neighbors corresponds approximately to the minimum of this lowest band. In this state, the occupied zones do not overlap the unoccupied ones, and the solid is a nonconductor.

The energy spectrum of diamond differs from that of the metals in that in the former a peculiar separation of the zones occurs after they have overlapped. This separation implies, from the point of view of the wave theory, a concentration of the electronic charge along directions between nearest neighbors. In other words, the electronic distribution in valence crystals is less isotropic than in metals. This localization was recognized quite early in the history of valence theories, and gave rise to the very useful concept of the shared electron pair. Actually, the directional localization is never entirely complete, even in diamond.

If the most stable state had occurred at a larger distance, before the eight zones separated into groups of four, it is clear that the solid would have been a metal. This suggests an explanation for the metallic properties of graphite. In the graphite lattice, the atoms in a given layer have a very close distance of approach (1.42A), but the layers are quite far apart (3.69A). In diamond, contrastingly, each atom has four nearest neighbors disposed at the corners of a regular tetrahedron. The band system in graphite will thus correspond roughly to a mean of that shown in Fig. 21 for large and small distances, and this implies that all eight zones overlap, with resulting conductivity.

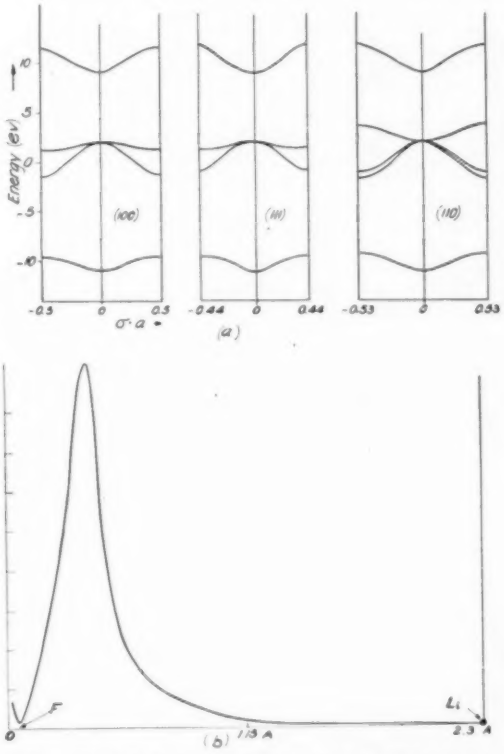


FIG. 20. (*a*) Relative scale plot of the allowed and unallowed energy regions for three prominent directions in LiF. (*b*) Relative scale plot of the valence charge distribution between neighboring F and Li nuclei.

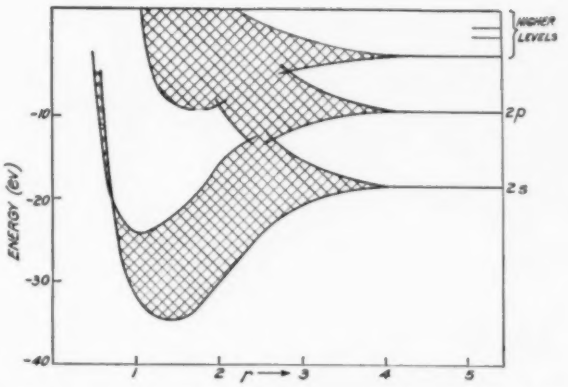


FIG. 21. Semi-quantitative representation of the zone scheme of diamond, varying with lattice spacing.

Si has the same electronic structure as carbon, and a common modification crystallizes in the diamond lattice. We should expect the band system arising from the 3*s* and 3*p* atomic states to be qualitatively the same as in diamond. The atomic levels are spaced much closer in Si, however. Consequently, we cannot expect the two bands into which the eight zones split to be as far apart in Si as in diamond. Actually, Si is a very poor conductor at very low temperatures, in agreement with the first of these predictions. At higher temperatures it acquires a feeble electronic conductivity which increases with temperature, in agreement with the second prediction.

Carborundum is another substance like diamond and Si, differing from these only in that there are two different atoms in the unit cell. The Si 3*s* and 3*p* atomic states are above the 2*s* and 2*p* states of carbon. As the lattice is contracted the bands arising from the 2*s* and 3*s* states merge and then separate to form two

bands s_I and s_{II}, one of which goes down while the other rises, as in ionic crystals. The $2p$ and $3p$ levels combine in a similar way to form p_I and p_{II} bands, each containing three zones. s_I and p_I then overlap to form a band, corresponding to the lowest in diamond, which contains four zones and is completely filled. This overlapping of s_I and p_I is practically the same as the overlapping which happens in MgO, BeO, etc. (distance B in Fig. 19). We see that there is no sharp discontinuity between ionic and valence types. We may expect BeO, for example, to have some directional localization of electronic charge, and SiC to have some ionic properties. Since the carbon atomic levels are lower than those of Si, we should expect the electron concentration to be greater about the carbon. The unit cell would therefore have a dipole moment, as in ionic crystals. The strong infrared absorption spectrum of carborundum is qualitative evidence for the existence of this dipole moment.

(4) *Semiconductors*[5]

The interpretation of semiconductors on the basis of zone theory is obvious: these are solids in which the spacing between bands is so small that there may be appreciable thermal excitation of electrons from the filled to the unfilled bands. The conductivity σ, on this view, depends on E, the energy gap between the filled and unfilled bands, and on the temperature T, in accordance with the relation

$$\sigma = Ce^{-E/(2kT)}, \qquad (2)$$

as may be readily shown; k is Boltzmann's constant, and C is a factor which varies relatively slowly with temperature. It is obvious that the excited electrons are practically uninfluenced by the exclusion principle, because they are in a band with a large number of vacant states, so that they are readily available for conduction when a field is applied. We note that the nearly-filled lower band from which these electrons have been thermally excited can also assist in conduction, since it now contains some vacant states. The factor 2 in the denominator of the exponent in (2) enters because of this additional conductivity.

The expression (2) closely resembles that for ionic conductivity in solids. In the ionic conductivity, the energy $E/2$ in (2) is replaced by the energy with which an ion is bound in its position in the lattice. For some semiconductors, the two may be of the same order of magnitude. Ionic conductivity can be distinguished from electronic, at least in principle, by the fact that it results in electrolytic decomposition of the crystal, while electronic conductivity does not.

According to (2), since E is always finite, all nonconductors should become electronic conductors at sufficiently high temperatures. The magnitude of the energy gap E varies widely among the substances which are classed as semiconductors at room temperature. There is, in fact, a continuous gradation between insulators and metals, and any sharp distinction has to depend on arbitrary definition.

We find, for example, that monatomic solids of the same valence group become better conductors with increase in atomic number. Thus, diamond is a nonconductor, silicon is a semiconductor, germanium is a fairly good conductor and is classed as a metal, and tin is definitely metallic. The atomic states become closer spaced as we go down any given valence group, so that overlapping of the corresponding bands in the solids becomes more and more pronounced.

Diatomic compounds show the same behavior as the elements involved increase in atomic number, and for the same reason. BeO and CuO are good insulators, while CdS, Cu_2O and ZnO are increasingly better semiconductors. Finally, the alloys of metals are either fully metallic or good semiconductors. A qualitative prediction about the degree of electronic conductivity a substance will show can be made by examining the spacing among the energy levels in the constituent atoms. If the spacing is large, the substance will in general be a poor conductor (unless the unit cell happens to contain an odd number of valence electrons), and if it is small the metallic properties will be relatively pronounced.

Some numerical values of E are listed in Table II[6] for a representative set of monatomic and diatomic solids. C is of the order of magnitude of 1 ohm^{-1} cm^{-1} in all cases, and is difficult to determine accurately.

One important property of semiconducting crystals remains for consideration, namely, their frequent transgression of the valence rules. We

TABLE II. *Energy gap E in electron volts.*

C (diamond)	7	Cds	0.7
B	2	Cu_2O	0.6 to 0.2
S	0.7	CuO	0.5
P (white)	1.2	ZnO	0.4 to 0.0
P (black)	0.2	WO_3	0.3
		UO_2	0.25
		CuS	metal

note, first, that the energy level spectrum of a substance like diamond is characterized by the separation of a band of four zones from the rest of the system, so that eight electrons can be tightly bound. This separation arises primarily from the wide spacing of the atomic energy levels, and is connected with the localization of the electronic charge along particular directions in the solid. Since all light elements have a wide spacing of atomic levels, we may generally expect four low lying zones in a lattice in which there are equidistant neighbors, and hence a "rule of eight." It may happen that the atoms will form a different lattice (graphite, for example, instead of diamond) in which the four levels do not separate off from the rest of the spectrum. The rule of eight is violated when such a modification exists. In elements of higher atomic number, whose atomic energy spectra are increasingly dense, the overlapping of bands in the solid becomes more pronounced, the separating-off of four low zones is therefore less pronounced, and the significance of the octet rule is gradually lost. In other words, there may be more or fewer than eight electrons per unit cell in the stable configuration because there are more or fewer than four low lying zones. One would expect this tendency toward formation of "anomalous" lattices to be most apparent where overlapping is greatest—that is, in the metals. And, in fact, the "combining ratios" of alloy systems are difficult to interpret by ordinary valence rules. The significance of the Hume-Rothery rule will be mentioned later (V, 3).

(5) *Molecular Crystals*

We have already attributed the insulating properties of these crystals to the narrowness, at the equilibrium spacing, of the bands arising from electronic energy levels in the molecule as the lattice is contracted. It is implied, of course, that the bands are filled, and this is guaranteed by the fact that the molecules have saturated valences.

In the binding energy of a molecular crystal, computed on the zone basis, it turns out that the correction terms (see III, 4) are all-important. The correlation term varies inversely with the sixth power of the intermolecular spacing, and is, in fact, just the van der Waals interaction energy. The exchange term, favoring repulsion in this case, increases very rapidly with decreasing distance, and equilibrium results at a spacing at which the energy bands are very narrow. All the other electronic terms, because of the narrowness of the bands, are practically the same for the crystal as for the isolated molecules.

We may remark that the valence laws for molecules are interpreted, from the quantum-mechanical viewpoint, in the same way as for solids (see IV, 4) and have the same range of validity. The simple octet rule, in molecules as in solids, cannot be expected to hold strictly when the atoms involved have dense energy spectra. In a crystal composed of molecules containing such complicated atoms, other terms in the cohesive energy may become important—the forces between molecules may become comparable with the forces between atoms in the molecule. In the solid, in short, the molecules lose much of their "molecular character."

We emphasize once more that the classification of solid types we have been using is highly arbitrary. In nature, gradations exist between any one type and any other. In the group of solids NaF, MgF_2, AlF_3 and SiF_4, for example, there is a transition from a "pure ionic" lattice with high melting point, good electrolytic conductivity, etc., to a low melting crystal with typical molecular properties.[7] The various features of the general theory, correspondingly, shift gradually in relative importance as the theory is applied to the successive members of such a group.

V. The Zone Theory and Volume Properties

(1) *Heats of Sublimation; Thermal Properties; Phase Changes*

The difficulty of computing heats of sublimation has been discussed in the first article (see III, 4). When the "variational procedure" is

TABLE III. *Representative heats of sublimation (kcal./mole).*

	COMPUTED	OBSERVED
NaCl	175	183
Li	23	26
Na	34	39

followed, good agreement between observed and calculated values means that a fairly good picture of the solid has been used—fortuitous agreement is ruled out. The computations have been made for the simpler metals and ionic crystals.[8] The results (Table III is representative) include, of course, the exchange and correlation corrections to the zone picture of electronic motion, but the agreement shows that the zone theory is a good first approximation. The calculations are almost prohibitively laborious, and extension to more complicated substances is therefore slow. An excellent start has been made with diamond and the noble metals, Cu, Ag and Au.

In determining thermal properties of solids, such as specific heat, the energy states of nuclear vibration are more important than the electronic energy states. When both are known, entropies, free energies, etc., can be computed by the methods of statistical mechanics. Einstein, Debye and others made considerable progress in this direction before modern quantum theory, neglecting the electronic part of the problem. The recent advances include this correction, and also deal with the vibrational energy spectrum in a more exact fashion.[9] Vibrational waves in a lattice are formally similar to electronic waves, and the zone method of description proves useful for vibrations, also. The modern treatment of the vibrational spectrum, in method and in type of success, is an extension of Debye's treatment in much the same way as the zone theory is an extension of Sommerfeld's picture of the electron gas.

Two sorts of phase change are distinguished. Changes of the first kind, typified by ordinary melting, occur abruptly at a definite temperature. The following is a suggested explanation of the sharp transition temperature. Suppose the crystal is regarded as a *single atomic system*, and the two phases A and B as two separate states of the system, with energies E_A and E_B and entropies S_A and S_B, respectively. Then, from a general theorem of statistical mechanics, the probability P_A that the system be in the state A is related to the probability P_B that it be in the state B by the equation

$$P_A/P_B = e^{-\{(E_A - S_A T) - (E_B - S_B T)\}/kT},$$

where k is the atomic Boltzmann constant. The numerator of the exponent, the difference in free energy of the two states, is of the order of calories, except in the narrow temperature range where its sign reverses. The denominator, kT, is only about 10^{-20} calories at ordinary temperatures. Consequently P_A/P_B is practically either zero or infinite except in the small temperature range where the difference between the free energies is about 10^{-20} calories (Fig. 22). This interpretation of sharp transition temperatures involves, in its use of the Boltzmann constant, an essential principle of the zone theory, that the crystal is a single atomic system.

The second sort of thermal transition, typified by the disappearance of ferromagnetism, and of the secondary structure in alloys, occurs continuously up to a sharp "Curie temperature" at which the transition is complete (Fig. 23); in some cases there is a gradual change followed by abrupt completion at the Curie point. On the view just outlined, these transitions take place through a number of intermediate states, the free energy of each state differing but little from

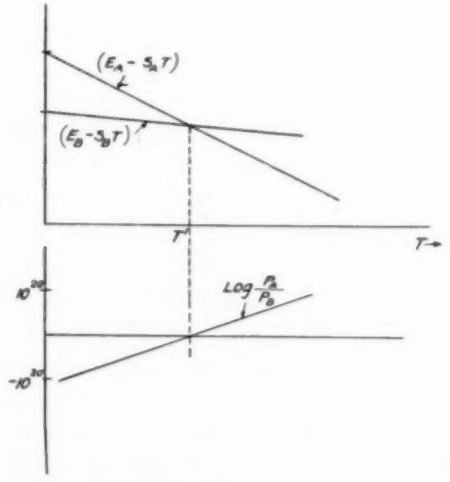


FIG. 22. Above: Schematic representation of free energies for two phases A and B, over a range of a few degrees about the transition temperature T'. Below: Corresponding variation of log P_A/P_B. Note that P_A/P_B is approximately unity only in a very narrow range about T'.

that of a state immediately preceding or following it. Recent theoretical investigations of these "order-disorder" transitions[10] have related them to the variation of the entropy of the solid with its energy.

(2) *Elastic Constants*

Evaluation of elastic constants follows approximately the same methods, and meets the same difficulties, as evaluation of the binding energy. The quantity required is the change in total energy when the crystal is distorted from the equilibrium arrangement. The simplest distortion to handle theoretically is one in which all

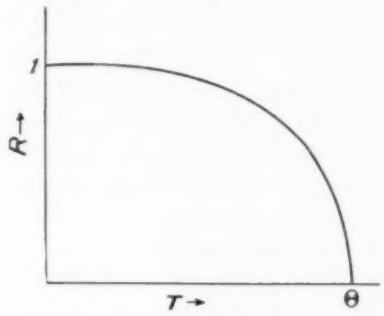


FIG. 23. Decrease in order of an alloy, from complete order ($R=1$) at 0°K to complete disorder ($R=0$) at the Curie temperature Θ.

interatomic distances are changed by a constant factor; from the energy change the compressibility can be computed. Fair agreement between computed and observed values has been obtained for NaCl[11] and for several metals[12] (Table IV).

The classical theory of ionic crystals assumed that the elastic forces are static forces of interaction between pairs of lattice points. For crystals having central symmetry, this assumption led directly to certain equalities among the elastic coefficients connecting stress components with strain components. Experimentally, these *Cauchy-Poisson* relations are not nearly true except for monovalent ionic crystals, and even there the discrepancy[13] is about 10 percent. Their general failure is easy to predict on the zone theory, since the interactions that determine the total energy as a function of lattice spacing are not static, but are dynamic, involving moving electrons. On the other hand, the modern theory, as we have seen, partly supports the classical picture of ionic crystals; the difference between the two, which is connected with the width of the electronic energy bands, would affect the elastic constants of the alkali halides by about the observed 10 percent.

TABLE IV. *Representative compressibilities* ($kg^{-1}\ cm^2$).

SOLID	COMPUTED	OBSERVED
Na	16	9 ($\times 10^{-6}$)
Cu	0.69	0.70 ($\times 10^{-6}$)
NaCl	8.4	4.24 ($\times 10^{-12}$)

(3) *Crystal Structure*

Generally, a solid crystallizes in the structure for which the free energy is least. The coexistence of allotropic forms is presumably due to the fact that the time required for transition to the lowest state may be very long. Thus, diamond and graphite both exist at room temperature, though one must be energetically more stable than the other. Explanation of such cases involves the absolute rate of chemical reaction, and the theory[14] has not yet been so fully developed that it can easily be applied.

The general fact, that the energy of the stable lattice differs very little from that of other configurations, makes present-day predictions of lattice structure almost futile. With the best methods of approximation now available, the cohesive energy computed on the zone theory is rarely accurate to better than 5 kcal./mole, and the difference in energy between a stable and a quite unstable lattice may be much less than this. The correct sign of this difference is usually the most that can be expected.

In the classical Madelung-Born theory of ionic crystals[15] the lattice energy was determined solely by static central-force interactions between pairs of ions. Two terms were used to represent the energy: a Coulomb term of the type e_1e_2/r, attractive for unlike ions, repulsive for like ions; and a term of the type $1/r^n$, repulsive whatever the signs of the pair of ions. This latter term corresponded to the impenetrability of the ions, and n was chosen large enough to make this term negligible for r large, but very large for r less than the observed lattice spacing. The zone theory, as we have seen, indicates that the lattice energy should include other terms, which arise from the finite width of the energy bands occupied by the valence

electrons, and which do not depend solely upon the distance between lattice points. These terms are smallest, and the central-force assumption therefore most nearly valid, in the alkali halides. However, the classical theory could not explain why the Li, Na and K halides are face-centered, while the Cs halides are body-centered. We must conclude that, even in the monovalent ionic crystals, the small noncentral terms in the energy have an important part in determining the stable configuration. These terms constitute approximately 10 percent of the total binding energy, and their quantitative treatment is still unfortunately rough. Qualitatively, the modern theory removes the difficulties, but the necessary quantitative calculations have not yet been made.

In the simpler metals the energy of the valence electrons is almost independent of the lattice structure, but depends strongly on the volume of the unit cell. This fact follows from the relative isotropy of the electronic charge distribution, which is associated with pronounced overlapping of zones. From it, two predictions are immediately possible: the actual structure will be a simple one, since there is little anisotropy in the individual atoms to require an anisotropic lattice; and the stable lattice will differ very slightly in energy from other simple configurations. Fuchs[16] has recently found, using the zone theory, that in the alkali metals and the noble metals (Cu, Au and Ag) the structure is determined, between face-centered and body-centered, by the small deviations of the ion-ion interaction from a simple Coulomb repulsion. His calculations indicate a greater stability of the face-centered lattice for the noble metals. However, the body-centered structure of the alkalis is not yet explained.

The empirical Hume-Rothery rule, which is obeyed in a variety of alloys, states that similar phase patterns occur at the same ratio of valence electrons to atoms. Jones[17] has shown how this rule is to be explained with the zone model. The number of valence electrons in the crystal is determined by the composition of the alloy, while the energy spectrum which they occupy is determined by the arrangement of atomic sites in space—by the phase pattern—regardless of which kind of atom is in each site. The most stable phase pattern is one which gives an energy spectrum with enough low energy states to accommodate all the valence electrons. The stable pattern is dictated by the number of valence electrons in the entire crystal. It fixes, in turn, the number of atoms in the unit cell, and thus the number of atoms in the crystal. Consequently, the same phase pattern recurs at a definite ratio of valence electrons to atoms.

The possibility of a metallic modification of solid hydrogen has recently led to a calculation[18] of the energy of simple monatomic lattice types. The results show that metallic hydrogen, at ordinary pressures, would be less stable than the molecular crystal, by about 1 ev per atom. Whether this difference changes sign at higher pressures is not yet known.

(4) *Mechanical Properties*

Such properties as hardness, malleability, and strength are not entirely volume characteristics, but may depend tremendously on the purity of the sample, its polycrystalline structure, and its surface condition. Hence, most of the detailed experimental knowledge is hopeless of interpretation in the present state of the theory, which deals with a perfect lattice. We shall have to consider only general comparisons among idealized materials.

The high malleability of pure metals, and particularly the softness and plasticity of the alkalis, appears to follow naturally from the fact that the electronic energy of simple metals is a function rather of the volume of the unit cell than of its shape. Thus, a deformation can occur with small change of energy.

The difficulty of cleaving a perfect crystal varies, obviously, with the energy of the new surfaces formed. The classical theory predicted, in agreement with observation, that face-centered ionic crystals should cleave most easily along (100) planes, less easily along (110) planes, and still less easily along (111) planes. Fig. 24 shows the reasoning directly. The ions on one side of a (100) plane alternate in both directions on the surface, and the attractive forces are largely balanced by repulsive forces. In the (110) plane the distribution alternates in one direction only, while in the (111) plane all the ions on one side have the same sign. This simple ex-

planation is taken over bodily into the modern theory, with the reservation that it applies only to those crystals (the monovalent and possibly some of the divalent ionic solids) where the binding energy is determined mainly by Coulomb ion interactions. Its use, for example, with metals, probably requires circumspection. We should not expect good cleavage in a crystal such as diamond, for there are many valence bonds crossing even the most favorable plane in the lattice, and the actual cleavage is likely to be determined by random flaws at which stresses accumulate. The notion that the electronic part of the cohesive energy is localized with the electronic charge distribution, is justified when we remember that the charge is localized so as to minimize the energy, and work has to be done to make it assume some other distribution, as it must when the crystal is split.

The first stage in the deformation of a pure single-crystal metal rod under tension is usually a gliding along certain lattice planes.[19] Since gliding exposes new surface, the surface energy is involved in determining which planes are glide planes; these surface energies have not been computed, because of mathematical difficulties. The accumulating distortions which accompany gliding and make it irreversible must, along with the other phenomena of cold work, be left for later mention.

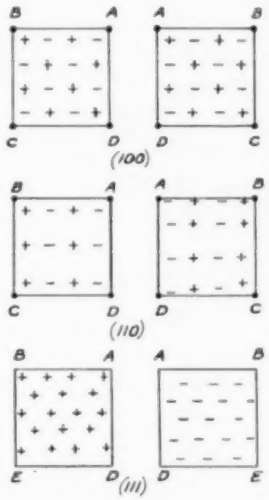


FIG. 24. Arrangement of ions on opposite sides of simple planes in a crystal such as rocksalt. The difficulty of cleavage increases in the order (100), (110), (111).

(5) *Optical Absorption*

A solid will absorb any light which (1) stimulates lattice vibrations or (2) excites electrons to states of higher energy.

The first kind of absorption, usually in the infrared, occurs whenever there is a mode of lattice vibration resulting in a dipole moment. Thus, NaCl has a dipole moment when the Na ions as a group are displaced relative to the Cl ions, and it will absorb light of the frequency of this mode. In diamond, contrastingly, all atoms are equivalent in location and in charge; no regular displacement of pairs gives rise to a dipole moment, and no infrared absorption would be expected in a pure sample.[20] A detailed prediction[21] of the structure of any infrared absorption spectrum requires a thorough treatment of the lattice vibrations on quantum theory, and no more than semiquantitative results have thus far been obtained.

From the existence of practically continuous bands of energy levels for the valence electrons in solids, it is not unreasonable to expect continuous bands in the optical absorption spectra, corresponding to excitation of valence electrons. Such bands are in fact observed in the visible and ultraviolet regions. Their structure can be predicted from the distribution and population of the energy levels, by applying quantum selection rules. The rules for volume absorption are very restrictive: an electron in a given state cannot be excited to any state in the same zone, and can be excited to but one state in any other zone—the particular state which has the same wave number vector σ as the original state. This means, roughly, that the momentum of the electron is conserved in the absorption process, the momentum $h\nu/c$ of the photon being negligibly small. The usual energy relation, $h\nu=\Delta E$, must of course also be satisfied. In the reduced zone scheme, the only allowed transitions are vertical (see Fig. 25): the lowest energy quantum that can be absorbed has energy equal to the smallest vertical energy difference between occupied and unoccupied states in different zones. Thus, in a metal in which zones overlap, the lowest frequency in volume absorption is not zero, since the neighboring energy functions are not equal for the same value of σ. When the zones are disposed as in Fig. 26a (typical for simple metals) the first electrons to be excited are those of highest energy, but in the case shown in Fig. 26b electrons of lower energy will be first excited. The theoretical threshold for Na and for Li is about 2 ev.

In the simpler metals the energy states are

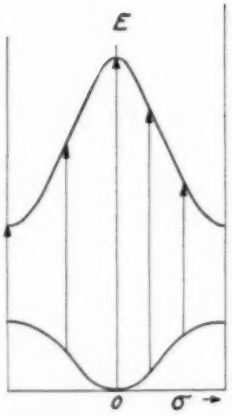


FIG. 25. Illustrates the electron transitions, vertical in the reduced zone scheme, which are allowed when the excitation is by absorption of light.

most dense near the top of the lower zone and near the bottom of the upper zone (Fig. 26a). There should therefore be a maximum absorption of quanta of energies near B, close to the absorption threshold A. With increasing frequency the absorption due to excitation to the first unoccupied zone should die down and be followed by a minimum, possibly by a region of transparency, before the conditions for excitation to the second unoccupied zone are fulfilled. The zones become very dense in the range of higher energies, because the higher atomic levels are closely spaced, so the minima of absorption will become less and less pronounced as the frequency increases. The predicted volume absorption spectrum has the general shape shown in Fig. 27 (full curves). The observed spectrum differs slightly from this at low energies because of weak surface absorption. The dotted curve (greatly magnified) shows the usual shape of this surface component, which is important for the photoelectric effect. Wood[22] finds that in the alkali metals there is a region of transparency preceding A in Fig. 27. This transparency cannot be easily detected in the visible because of the high reflecting power of metals. Insulators and metals should have approximately the same sort of volume absorption spectra, and a general similarity is experimentally observed. The threshold for insulators is usually farther in the ultraviolet, because the filled and unfilled zones are separated by a wider gap.

At very short wave-lengths (below about 100A) excitation of electrons in the outer closed shell of the ion core becomes predominant over excitation of valence electrons, and the simple zone treatment is no longer applicable.

(6) *Photoconductivity*[23]

Many insulators, when they absorb light, acquire a temporary feeble conductivity. This property seems immediately explicable on the zone theory: a few of the valence electrons are optically excited to nearly-vacant zones, where they are little influenced by the exclusion principle, and can carry a current—optical excitation in photoconductors simply replaces thermal excitation in semiconductors, and conductivity should be present whenever optical absorption is present. This explanation fails, however, to fit the observation that as the insulating substance is purified its photoconductivity becomes very small, while the absorption persists almost unchanged. This fact has long been known for the halides, and recent experiments[24] show that it is probably also true

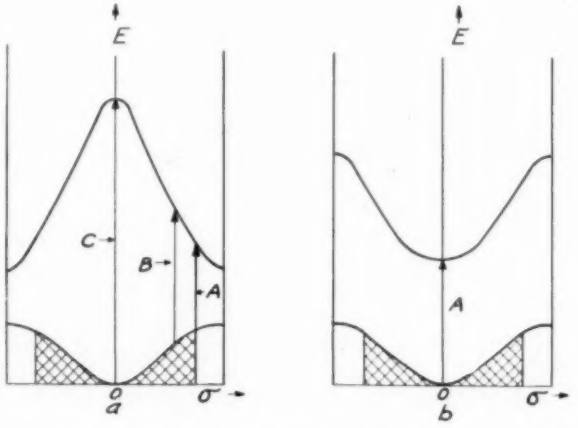


FIG. 26. The shaded regions indicate occupied levels of the lower zones. In (*a*) optical absorption near the threshold A results in excitation of the electrons in high energy levels; in (*b*) electrons of low energy are excited first. In (*a*) many transitions of the type B are possible, and an absorption peak near the threshold is to be expected.

for diamond, previously considered a typical "idiochromatic" crystal, photoconducting in the pure state.

The experiments have apparently all been confined to wave-lengths above 2500A where sources of high intensity are available.

Absorption without photoconductivity, in crystals supposedly pure, requires either that the absorption is due to undetected impurities, lattice flaws, or other entities that do not yield free electrons; or else that the zone theory is seriously in error in its treatment of absorption in the near ultraviolet. The second possibility has been discussed by Slater and Shockley,[25] with the tentative conclusion that optical ab-

sorption may have a sharp peak near the threshold, without accompanying photoconductivity (Fig. 28). After such absorption, the excited electron and the "positive hole" it leaves in the lower band are considered as traveling through the lattice together. The stability of such a neutral pair in an electric field has not been investigated. Further theoretical work, and extension of the experiments to shorter wavelengths, are both needed.

(7) *Metallic Conduction*

We saw in the preceding article that the fundamental difference between conductors and insulators is a natural consequence of the zone type of energy spectrum. In the field of metallic conduction, the modern theory has to its credit two important advances over the Lorentz and Sommerfeld theories: the explanation of the temperature dependence of conductivity, and the explanation of the anomalous galvano-magnetic effects.

Experimentally, the conductivity of most pure metals varies as $1/T$ near room temperature, but rises rapidly with decreasing temperature, and at very low temperature varies approximately as $1/T^5$. This sort of dependence was difficult for the free electron gas theories. They led to an expression for conductivity of the form

$$\sigma = \text{const} \frac{e}{m} \frac{nl}{v_{\text{ave}}}$$

where n is the density of free electrons, l is the mean free path (partially elastic collisions with lattice ions were imagined), v_{ave} is the average thermal velocity, and e/m has the usual meaning. On the Lorentz theory, v_{ave} varied as $T^{\frac{1}{2}}$; on the Sommerfeld theory it was practically independent of T. The observations required that either n or l should increase rapidly with decreasing temperature, and neither possibility appeared plausible. In the wave-picture, on the other hand, a perfect lattice should have zero resistance—the "mean free path" is infinite. Resistance is due to scattering of the electron waves at breaks in the periodicity of the lattice. At any temperature above 0°K, the thermal vibrations of the lattice ions destroy the perfect periodicity. When the scattering problem is worked out quantitatively, the observed variation of resistance with temperature is checked nicely (see Fig. 6). We note that an impurity atom in the lattice will also disturb the perfect periodicity, even at 0°K, and thus will cause scattering and electrical resistance. This gives an explanation of the high resistance of certain alloys, and of Mathiessen's rule, that the resistance of a dilute solid solution is the sum of the normal temperature-dependent resistance and another term which increases with concentration of the solute and is almost independent of temperature. Obviously, explanation of detailed differences in resistivity among different metals requires a detailed study of the electron energy spectrum and of the lattice vibration spectrum.

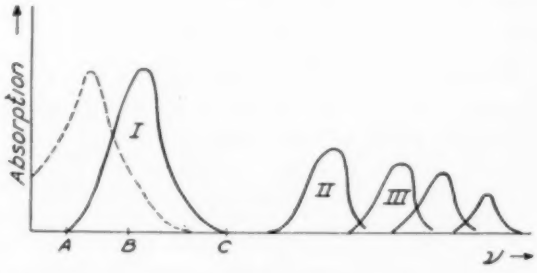


FIG. 27. Predicted volume absorption spectrum of a metal. The peaks I, II, III, etc. correspond to transitions to the first, second, third, etc. unoccupied zones. The dotted curve (magnified about 500 times) represents absorption at the surface.

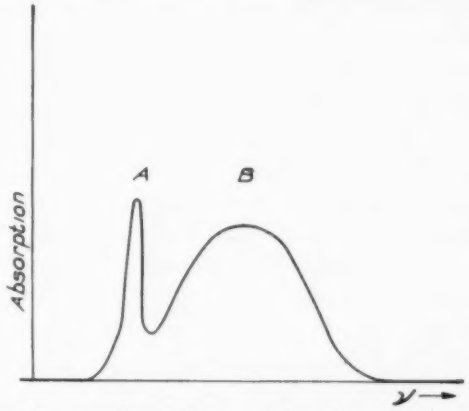


FIG. 28. Possible behavior of volume absorption in alkali halides near the threshold, as suggested by the work of Slater and Shockley. Electrons excited by absorption represented by the peak A are correlated with the "positive holes" they leave in the lower zone; excitation corresponding to B is not accompanied by such marked correlation. Absorption of the type A need not cause the crystal to become photoconducting.

The best known of the galvano-magnetic phenomena is the Hall effect. If a strip of metal

carrying current in the x direction is placed in a magnetic field in the y direction, a small electric field, the Hall gradient, arises in the z direction. In some metals—Zn, Cd and Pb, for example, the direction of this gradient is as if positive particles, rather than electrons, were carrying the current. This anomalous Hall effect turns out to be characteristic of metals in which the highest zone containing electrons is nearly, but not quite, filled. It is a consequence of the fact that energy states near the top of a zone correspond to a *lower* group velocity (the group velocity of the wave is a measure of the velocity of the electron, considered as a particle) than do states of lower energy in the same zone. A detailed treatment of the behavior of electrons in a nearly filled zone reveals the convenient fact that, in all its interactions with electric and magnetic fields, the metal behaves as if the few unfilled states near the top of the zone were filled with positive particles, of mass comparable with the electronic mass, while the lower filled states are vacant. In the anomalous Hall effect, these positive "holes" move toward the negative electrode; since their charge and velocity are both different in sign from those of a free electron, their course in the magnetic field is bent in the same sense as the course of an electron would be, and a reversed Hall gradient results.

We shall not attempt to review here the striking properties of the superconducting state[26] into which many metals pass, at a sharp transition temperature, characteristic of the metal, near 1°K. Many of the concomitant effects can be interrelated by the use of thermodynamics and electromagnetic theory, but a wholly satisfactory picture of superconductivity has not yet been found. Slater[27] has very recently presented a promising viewpoint. He considers the energy states of the metal as a whole, and finds evidence for the existence of a set of discrete states which would correspond to the superconducting phase. These ideas cannot be adequately discussed on the zone approximation.

(8) *Magnetic Behavior*

We have space for only a bare mention of the viewpoint of the modern theory regarding the magnetic behavior of solids. As in the classical theory, diamagnetism is explained as due to the orbital motion of the electrons. Paramagnetic behavior is attributed to the magnetic spin-moment of "unpaired" electrons. (See II.) In any solid, these two tendencies are in opposition. Where the electron spins are permanently paired, as they are in insulators with filled zones, only the diamagnetic tendency is present. The strong paramagnetism of the rare-earth salts is interpreted as due to the presence of the unfilled inner f shell in the atom. The problem of ferromagnetism is being attacked on the basis of a suggestion by Heisenberg, that the spontaneous alignment of the elementary magnets is a result of the exclusion principle. It seems likely, however, that a completely irreproachable solution will not be had until the methods of approximation are greatly improved. The reader is referred to the volume by Mott and Jones (Chap. VI) for a fairly complete discussion of the modern interpretation of magnetic phenomena in various metals.[28]

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27. Slater, Phys. Rev. **51**, 195 (1937).
28. See also Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932); Stoner, *Magnetism and Matter* (London, 1934); Bozorth, Elec. Eng. **54**, 1151 (1935); Slater, Phys. Rev. **49**, 537 (1936).

One peculiarity of scientific research is that its results can usually not be foreseen, for if they could be foretold they would not be new. Also, when a new discovery is made, it is not usually immediately obvious as to the possibilities of its practical uses. And again, the solution of a scientific problem may be a long, hard struggle—longer than was realized by a visitor who asked Harvard's President Conant what he was doing in his laboratory. When Conant replied, "We are seeking to discover the chemical formula for chlorophyl," his visitor exclaimed, "Why, how is that? You were working on that problem when I was here last year!"

Because of these uncertainties I can not predict just what the next big scientific developments will be, but I can assure you that they will come and that they will be important. Among the fields that seem to me to show especial promise are: development of new industrial uses for farm products; improvements in transmission and utilization of electric power; great developments in materials and methods of building construction; increased range and precision of weather forecasting; conquest of hitherto unconquered diseases, both physical and mental; better regulation of bodily functions; a new era in biological discovery operating with the tools of physics, chemistry and engineering; a similar new era in physical science centered around atomic nuclear transformations; and so on, the field is literally limitless.

—KARL T. COMPTON—"Science in an American Program for Social Progress," *Scientific Monthly*

Here and There

¶ An Electronics Institute, consisting of a special lecture and conference program in electronics will be held in Ann Arbor, Michigan, as a part of the 1937 Summer Session of the University of Michigan, with the cooperation of members of the technical staffs of the General Electric Company, the Westinghouse Electric and Manufacturing Company, and the Bell Telephone Laboratories.

The Institute lectures will be given by Dr. Saul Dushman and Dr. Lewi Tonks of the General Electric Research Laboratories, Dr. H. E. Mendenhall and Dr. F. B. Llewellyn of the Bell Telephone Laboratories, Dr. Joseph Slepian and Dr. R. C. Mason of the Westinghouse Research Laboratories, Professor L. B. Loeb of the University of California, and Professor W. G. Dow of the University of Michigan.

The lecture program will consist of two independent four-weeks lecture sequences, dealing, respectively, with high-vacuum (June 28 to July 24) and gaseous-conduction (July 26 to Aug. 20) electronic principles. In parallel problem laboratory and conference courses the lecture material will be worked into illustrative engineering problems, and teaching methods will be demonstrated and discussed. Opportunities for informal conferences will be provided.

Address Professor W. G. Dow, Electrical Engineering Department, University of Michigan, Ann Arbor, Michigan, for further information.

★

¶ A world congress on universal documentation will be held in Paris, August 16–21, 1937. The term "documentation" includes documents, printed or otherwise recorded manuscripts, and the necessary catalogues, indexes and bibliographies which provide ready access to any of the material. The proposed congress will consider the production, grouping, abstracting, and selecting of documents and the probability of cooperation between all centers of documentation.

Mr. Watson Davis, *Science Service*, Washington, D. C., is the American representative on the international committee.

★

¶ Dr. K. Fajans, professor of chemistry at the University of Michigan, addressed the Detroit Physics Club on January 19, 1937, on "Chemical Forces in the Light of Optical Investigation."

★

¶ Dr. R. A. Nielsen of the Westinghouse Research Laboratories spoke on "Electron Drift Velocity" at the regular meeting of the Physical Society of Pittsburgh, on February 11.

¶ *Nature* reports the following 1936 prize awards of the Paris Academy of Sciences: the L. La Caze Prize to Jean Becquerel, for the whole of his work in magneto-optics; the François Hébert Prize to Georges Albert Boutry, for his researches on photoelectric cells and their applications; the Hughes Prize to Marcel Laporte, for his researches on the electric discharge in gases; the Paul Marguerite de la Charlonie Prize to Henri Abraham, for the whole of his scientific work; the Clément Félix Foundation to Mlle. Nine Choucroun, for the continuation of her work on electrophoresis.

★

¶ The American Institute of Mining and Metallurgical Engineers announces several honorary awards. Erskine Ramsay, chairman of the board and general consulting engineer of the Alabama By-Products Corporation of Birmingham, Alabama has received the William Lawrence Saunders Gold Medal, "for his many inventions of all kinds of machinery and equipment used in bituminous coal mining and preparation; for effecting improvements in cokemaking that resulted in the establishment of the steel industry in Alabama; for skill in administering large enterprises; for unceasing aid to young engineers through personal efforts and benefactions to educational institutions."

J. Edgar Pew, vice president of the Sun Oil Company, has received the Anthony F. Lucas Gold Medal, "for his continuation and vigorous promotion of the program of standardization of oil field equipment; for his constant championship of the use of engineering principles and talent in oil field development; for his able work as an administrator of a great national industrial association in bringing about a more exact national understanding of the problems of the petroleum industry."

The following other awards have been made: George S. Rice, the Certificate of Honorary Membership in the Institute; William Floyd Holbrook, and Thomas L. Joseph, the Robert W. Hunt prize; John M. Hassler, the J. E. Johnson, Jr., award. These awards were made at the annual dinner, February 17, at the Waldorf-Astoria, New York.

★

The success of the Symposium on Metals is due in no small measure to the excellent arrangements made by Professor John C. G. Wulff of the Department of Physics, Massachusetts Institute of Technology. His enthusiasm lent a friendly spirit to the meeting which is often missing in scientific gatherings.

Symposium on Metals

¶ A Symposium on Metals was sponsored by the American Institute of Physics, January 28–30, in cooperation with the Massachusetts Institute of Technology. The meeting, held in Cambridge, attracted about two hundred physicists and metallurgists. The fundamental problems in the physics, chemistry and metallurgy of steel was the subject of the Symposium. Naturally, however, much of the discussion had a close bearing on problems of non-ferrous metals as well.

The objective of the sponsoring Institutes in arranging the symposium was to be of service to technical men in the steel industry in a somewhat unusual way. This meeting was a departure from the customary type of scientific meeting devoted to some particular branch of science or technology because it attempted to center the contribution of all fields upon an important application of science. The distinctions implied in the words physics, chemistry, metallurgy and the like were suppressed as far as possible in conformity with the fact that problems met by the steel industry do not obligingly conform to the artificial boundaries between such divisions.

The program ranged from the fundamental theory of solids derived from the modern knowledge of the atom, to specific practical problems which the steel industry is now studying. The arrangement of the program into a coordinated group of excellent papers was made possibly only through the able and enthusiastic efforts of Professor John Wulff of Massachusetts Institute of Technology. It was arranged in five half-day sessions as follows:

Thursday Morning

Chairman, Henry A. Barton, *Director, American Institute of Physics*

1. **The Electronic Structure of Alloys.** J. C. Slater, head, department of physics, Massachusetts Institute of Technology.
2. **Factors Affecting Diffusion in Solid Alloys.** R. F. Mehl, head, department of metallurgy, Carnegie Institute of Technology.
3. **Some Recent Experiments in Ferromagnetism.** Francis Bitter, associate professor of physics of metals, Massachusetts Institute of Technology.
4. **Stainless Steels.** V. N. Krivobok, associate director of research, Allegheny Steel Company.

Thursday Afternoon

Chairman, Walter G. Whitman, *Head of Department of Chemical Engineering, Massachusetts Institute of Technology*

5. **Corrosion.** R. M. Burns, assistant chemical director, Bell Telephone Laboratories, Incorporated.
6. **Pit Corrosion.** John Wulff, assistant professor of physics, Massachusetts Institute of Technology.
7. **Properties of Glass Sealing Alloys.** A. W. Hull, assistant director, Research Laboratory, General Electric Company.

Friday Morning

Chairman, John T. Norton, *Associate Professor of Physical Metallurgy, Massachusetts Institute of Technology*

8. **Flow Phenomena in Heavily Stressed Metals.** P. W. Bridgman, professor of physics, Harvard University.
9. **The Elastic Properties of Ferrous Alloys at Room Temperature.** A. V. de Forest, associate professor of mechanical engineering, Massachusetts Institute of Technology.
10. **On the Creep of Solids at Elevated Temperatures.** A. Nadai, consulting mechanical engineer, Research Laboratories, Westinghouse Electric and Manufacturing Company.
11. **The Mechanics of Rolling.** C. L. W. Trinks, professor of mechanical engineering, Carnegie Institute of Technology.

Friday Afternoon

Chairman, R. S. Williams, *Professor of Physical Metallurgy, Massachusetts Institute of Technology*

12. **Possibilities and Limitations of Spectrographic Analysis of Ferrous Materials.** G. R. Harrison, director of applied physics, Massachusetts Institute of Technology.
13. **The Use and Limitation of X-Ray Diffraction.** John T. Norton, associate professor of physics of metals, Massachusetts Institute of Technology.
14. **What Electrons Can Tell Us About Metals.** C. J. Davisson, research physicist, Bell Telephone Laboratories, Incorporated.

Saturday Morning

Chairman, G. B. Waterhouse, *Professor of Metallurgy, Massachusetts Institute of Technology*

15. **Hard Materials for Cutting Tools.** Zay Jeffries, technical director, Incandescent Lamp Department, General Electric Company.
16. **Minute Nonferritic Particles in Steel.** A. B. Kinzel, chief metallurgist, Union Carbide and Carbon Research Laboratories, Incorporated.
17. **Powder Metallurgy.** S. L. Hoyt, director metallurgical research, A. O. Smith Company.
18. **The Transformation of Austenite.** Edgar C. Bain, assistant to vice president, United States Steel Corporation.

On Friday evening a dinner of about one hundred was held in the Hotel Copley Plaza. This was an unusually pleasant occasion. After the dinner, Professor George B. Waterhouse, as Toastmaster, first introduced Dr. Karl T. Compton, president of Massachusetts Institute of Technology, who spoke about the underlying objectives of the meeting and their broad significance and value. The second speaker was Dr. Albert Sauveur, professor emeritus of metallurgy and metallography, Harvard University. Professor Sauveur's talk consisted of his reminiscences particularly of the early development of the subject of metallurgy and its industrial use. He closed his discourse with a series of portrait lantern slides of men who have made noteworthy advances in the sciences and technology of metals, citing each one in the manner in which honorary degrees are awarded.

On Saturday afternoon a number of researches in the laboratories of the Massachusetts Institute of Technology and of the Watertown Arsenal were inspected.

Insofar as judgment can be based on comments made to the several individuals who undertook the arrangement of the Symposium on Metals, it proved to be an exceptionally interesting and valuable meeting. This is the first of a series of conferences being planned by the American Institute of Physics. The Institute is anxious to introduce and increase the services of physics and related fields to industries. This general theme predominated in the Anniversary Meeting held by the five member societies in New York last October. That meeting embraced industrial applications generally. The Cambridge meeting singled out the ferrous metals industry. A number of proposals have been made for symposia on physics in such industrial fields as plastics, paper manufacture, motion picture production, food packing, and others. A tentative start has already been made on arrangements for two meetings next fall, one on bio-physics and one on physics in the automobile industry.

The papers from the Symposium on Metals will be published from time to time, in the *Journal of Applied Physics*. This journal will also be the natural place of publication of the papers to be presented at the future meetings.

¶ At the annual dinner of the American Institute of the City of New York, held on February 4, 1937, two awards were made. The Bell Telephone Laboratories received a gold medal in recognition of its outstanding accomplishments in research, more specifically "for researches in electrical science which, applied to communication, have promoted understanding, security and commerce among peoples by transmitting human thought instantly throughout the world." President Karl T. Compton of M. I. T. spoke of the accomplishments of the Bell Telephone Laboratories, and Dr. Frank B. Jewett accepted the medal in behalf of the 4500 employees of the Bell Telephone Laboratories.

Watson Davis was awarded a fellowship in the Institute for "interpreting to the people of the nation the rapid progress of science upon which modern civilization depends and for the organized dissemination of research findings as news."

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¶ A conference to review present and proposed methods for recording all research work was held in the National Academy of Sciences building in Washington, D. C., on January 16, 1937. The extension of the Bibliofilm Service of *Science Service* was given special attention. It was suggested that national scholarly agencies appoint delegates to attend a meeting to establish a Documentation Institute to be held in the near future.

¶ The Electrochemical Society, Inc., will meet April 28–May 1 at Philadelphia. Some of the subjects to be considered are "Electrochemical Methods in Biology," "Electrode Phenomena in Aqueous Solutions," "Industrial Catalysis" and "Photo-Cells." On April 29, Dr. D. W. Bronk will give a popular lecture on "Electrical Methods in the Study of Nerve and Muscle." Visits to manufacturing plants in the Philadelphia district are being arranged.

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CALENDAR OF MEETINGS

Acoustical Society of America

Washington, D. C., May 3–4, 1937

American Association for the Advancement of Science

Denver, Colo., June, 1937

American Chemical Society

Chapel Hill, N. C., April 12–15, 1937
Rochester, N. Y., September 6–10, 1937

American Physical Society

Washington, D. C., April 29–May 1, 1937
Denver, Colo., June, 1937
Madison, Wis., June 22–23, 1937

Among the New Books

The Theory of Lubrication. MAYO D. HERSEY. Pp. 152+ xii, Figs. 24. John Wiley and Sons, Inc., New York, 1936. Price $2.50.

It is pointed out in the preface that this book is composed almost entirely of verbatim or slightly modified reproductions of the author's own previous publications. As may be anticipated, the author has chosen for reproduction those of his papers which are essentially of an expository character and which had originally been prepared as reviews of particular phases of lubrication. For it is most unlikely that a subject which has engaged the attention of such men as Reynolds, Sommerfeld, Michell, Stanton, Kingsbury, Duffing, and Hardy should be subject to complete description in terms of the researches of a single individual. However, this in no wise lessens the value of the book, as there has indeed been a definite need for a descriptive review of the tremendous amount of work on lubrication that has accumulated during the last 35 years. The general nature of the contents may be inferred from the chapter headings, namely: "Historical Introduction," "Viscosity and its Relation to Friction," "The Classical Hydrodynamics," "Dimensional Theory, with Applications," "Temperature Rise in Bearings," and "The Problem of Oiliness." While the material chosen by the author for discussion is well presented, it seems that the words "Introduction to" might have been an appropriate addition to the title, so as to give a fair warning to the reader that he is to find mainly an outline of the problem of lubrication rather than a complete account of the present status of its solution. It is really unfortunate that the author has explicitly refrained from reviewing either the published experimental data on both thick and thin film lubrication or the techniques involved in obtaining these data. For it is largely in these that one finds not only the unsolved problems of lubrication, and the reasons for the divergences obtained by different investigators, but also because the experimental side of the subject of lubrication is probably in an even less satisfactory state than that of the theory. Perhaps, however, these various omissions may be condoned because of the unusually complete bibliographies following each chapter, which will provide the searching reader with all the additional material toward which his particular interest may be directed.

MORRIS MUSKAT
Gulf Research & Development Company

Electronics and Electron Tubes. E. D. McArthur. Pp. 173+vi, Figs. 89, Appendix. John Wiley & Sons, Inc., New York, 1936. Price $2.50.

As its preface indicates, this book is in large part a reprint of articles which have appeared serially in the *General Electric Review*. It may perhaps be assumed that much of the material was originally prepared to meet the needs of newcomers to the staff of the General Electric Company. For this it is admirably adapted. Its appeal to a wider audience is more limited. The physicist will find its theory too elementary and its practice too detailed to meet his needs. The electrical engineer who is not working in this field will find the theory too difficult and the practice insufficient. It may fairly be questioned whether anything else can be expected within the confines of two hundred pages. A treatise of twice this length might contain a treatment of the theory and practice of electronics and electron tubes which would be satisfactory to both groups of prospective readers. Those who have access to a well-stocked library will be able to supplement the material here given by consulting the excellent list of references provided at the close of each chapter.

The author's clear expository style and thoughtful provision of paragraph numbers suggest that this book might be used as an undergraduate class text. The teacher will have to supply derivations, correct a few misprints, and call attention to the inclusion of mixed units in formulas (cf. p. 5). The student will need a diagram of the resistance-coupled amplifier to accompany Chap. VI, and should be given a more extensive treatment of amplifier and oscillator circuits, perhaps at the expense of the admirable discussion of gas-filled tubes which occupies fifty pages. Thirteen excellent photographs of tubes would have been improved by the inclusion of a foot-rule, human hand, or other familiar object to give the scale of sizes represented.

Chas. Williamson
Carnegie Institute of Technology

The Theory of Metals, A. H. Wilson. Pp. 272, Figs. 31. The University Press, Cambridge and the Macmillan Company, New York, 1936. Price $5.00.

In this book the author has endeavored to give as precisely as possible a complete theoretical account of the electronic properties of solids, paying particular attention to the assumptions involved and to the difficulties which still remain. It is with this object in view that he has refrained in general from the quantitative discussion of particular models, except those of free or nearly free electrons. General theory is introduced in Chapters I and II. Chapter III is concerned with equilibrium properties such as the number of free electrons in metals, alloys and semi-conductors, together with the more difficult questions such as cohesion and diamagnetism. The optical properties of metals are dealt with in Chapter IV, while Chapter V gives a fairly complete account of the easier parts of the conduction theory. Chapter VI deals with the subject of the mechanism which produces the resistance in a metal, and the yet unsolved problem of superconductivity is discussed in Chapter VII.

Glances at Industrial Research. E. R. Weidlein and W. A. Hamor. Pp. 246+x, Figs. 25. Reinhold Publishing Corporation, New York, 1936. Price $2.75.

This book is intended to narrate the contributory relationship of the Mellon Institute to recent industrial research progress and to present the Industrial Fellowship System of that institution as a productive force in technologic advancement.

Electron Tubes in Industry. Keith Henney. Pp. 539+viii, Figs. 48. The McGraw-Hill Book Company, New York, 1937. Price $5.00.

In the second edition of this very usable book most of the recent applications of vacuum tubes are discussed. Industrial engineers, teachers and students will find many examples of the applications of amplifiers, oscillators, phototubes, rectifiers, thyratrons, grid-glow tubes, and cathode-ray tubes. References to books and serial publications are given so that anyone interested can easily find further details.

IX^{E} Congrès International de Photographie. Pp. 852. Published by L. P. Clerc, La Revue d'Optique Théorique et Instrumentale, Paris, 1936.

This is a report of the International Congress of Scientific and Applied Photography, held in Paris, July, 1935.

Ions in Solution. R. W. Gurney. Pp. 206, Figs. 45. The University Press, Cambridge and the Macmillan Company, New York, 1937. Price $3.00.

This book is a study of ions in solution upon the same basis that Dr. Gurney has used in recent research papers. The subjects treated in this volume are solvation energy, atomic and molecular ions, lattice energy, removal and deposition of metallic ions, assemblies of ions, interionic forces, cells and half-cells, successive degrees of ionization and equilibrium, dissociation, assembly of dipoles, exchange forces, solvation energy, electrochemical series.

Der Aufbau der Zweistofflegierungen. M. Hansen. Pp. 1100. Springer, Berlin, 1936. Price 66 R. M. or $27.32.

Scientific House Organs

Cenco News Chats, February 1937. There is an interesting article on "Physics and the Medical Sciences" in this issue. Also, one on a "New Rating Method for High Vacuum Pumps," as well as descriptions of the Cenco plant and new scientific apparatus. There is also a page of news notes. Central Scientific Company, 1700 Irving Park Blvd., Chicago, Ill.

Bausch & Lomb Magazine, February 1937. This issue contains articles on the design of proper bifocal lenses, Christian Huygens, Polaroid, Seeing and news events. Bausch & Lomb Optical Company, Rochester, N. Y.

Innovations in Instruments

New Standard Resistance Boxes

The Shallcross Mfg. Company, Collingdale, Pa., announce a new group of resistance boxes ranging from 1 ohm to 10 megohms which employ Shallcross nonreactive wire wound Manganin resistors. These instruments are intended for comparison standards for schools, colleges and industrial laboratories. Bulletin 812-A1 describes these new standard resistance boxes in detail.

New Cathode-Ray Oscillograph

The RCA Manufacturing Company announces a new oscillograph, with a one-inch screen at almost half the cost of the larger, more elaborate oscillographs. Its development was only recently made possible by using the new RCA 913 simplified cathode ray tube, and further simplification of the associated apparatus. With it, circuits may be accurately aligned, visually; all forms of distortion and hum checked, and modulation measured. Among its outstanding features are high sensitivity, providing full visual image while using only 1.75 volts (r.m.s.); vertical and horizontal amplifiers, with individual controls, in a flat range of from 30 to 10,000 cycles; linear timing axis in the same range; small spot diameter for sharp focusing and individual centering controls. It utilizes five tubes, and has an input power consumption of 50-watts cold and 30-watts hot.

Electronic Sweep Test Oscillator

A further new RCA development is a new electronic sweep test oscillator. It is a.c. operated and may be used with all types of cathode-ray oscillographs in alignment applications, eliminating the need for a separate frequency modulator. High output, negligible leakage, variable with frequency modulation, and a sweep rate of 120 times per second which eliminates flicker are some of its features. An easy-to-read 4-inch dial, rotating 340 degrees, spreads the six fundamental frequency ranges over a total scale length of 45 inches. Other specifications are five tubes; frequency range of from 90 to 32,000 kilocycles; output control has three-step attenuator plus continuously variable control; dimensions $13\frac{3}{4}$" in length, $9\frac{1}{4}$" high, $7\frac{1}{2}$" deep. and weighs 17 pounds.

Instruments for Spectrographic Analysis, Catalog D-20, 32 pp. This catalog contains much useful information in addition to that mentioned above. It seems as though it would be indispensable to anyone doing work in the field of spectrographic analysis. This booklet may be obtained from Bausch and Lomb Optical Company, Rochester, N. Y.

Balopticons and Accessories, Catalog E-11. This is a 24-page booklet giving tables for determining focal lengths of lenses for various screen sizes and the specifications for all of the projectors of this company. Bausch and Lomb Optical Company, Rochester, N. Y.

Spectrometric Equipment. Pp. 32. The following chapter headings are included: Basic Theory and Design, Direct Vision Spectroscopes, Bunsen Spectroscope, Laboratory Wavelength Spectrometer, Spectrophotometry and Quartz Ultra Violet Monochromator. Bausch and Lomb Optical Company, Rochester, N. Y.

Contributors to this Issue

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Contributed Original Research

Plastic Behavior of Metals in the Strain-Hardening Range. Part I

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(Received December 19, 1936)

The stress-strain relations for the cold working of the ductile metals are described for a group of cases assuming that the stresses under which they yield plastically depend only on the permanent parts of the strains, leaving out of the consideration the influence of the elasticity and of the speed of the plastic deformation. The behavior of the metals in the strain-hardening range is expressed by means of a strain-hardening function which connects the octahedral shearing stress with the octahedral unit shear. These variables are defined for strains of finite magnitude.

Introduction

IT is known that the stresses under which polycrystalline metals yield plastically, depend both on the plastic strains and on the rates with which these plastic strains change with time. It is evident that the treatment of the subject could be simplified considerably if one could consider one of these variables to be negligible in its effect, for example, by assuming a flow which is independent of speed or a flow in which the yield-stresses depend only on the plastic speeds of deformation but not on the plastic strains. Although unfortunately the experimental data do not quite support such a simple view in an important range of temperatures, it can be said that for the soft metals at low temperatures the first assumption is valid and that at elevated temperatures the effect of the speed of deformation becomes important. These two ranges of the temperature, although not sharply defined, have been characterized as the range in which a metal "strain-hardens" and in which it "creeps," respectively. At sufficiently low temperatures yield stresses need to be increased considerably to produce new plastic strains, while at elevated temperatures strains increase under a constant stress indefinitely and the metal flows the faster the higher the stress is.

That the speed of deformation does not need to be taken into account when certain metals are worked at sufficiently low temperatures is due to the logarithmic form of the law connecting stress with the velocity of flow. For certain ductile metals, at room temperatures there is little difference between the stresses required for the slowest and for the fastest rates of plastic flow encountered in practical applications or in tests. In other metals, however, which have low melting points and which start to recrystallize at room temperatures, the effect of the speed of deformation is very pronounced at room temperature (e.g. lead). Even in the case of some metals having high melting points, such as copper or mild steel, the influence of the speed of deformation upon the yield stresses is quite noticeable. A consequence of this is that under constant stress "creep" occurs at room temperatures[1] or that "relaxation of stress" occurs at constant strain. In spite of all these facts, it has become the practice for engineers to describe a group of phenomena related to the cold working of such metals as copper or mild steel first without introducing the effect of the speed of deformation and by assuming that the stresses required to stretch test pieces or to cold form sheets, bars,

[1] "The Creep of Metals," Part II, J. App. Mech. A.S.M.E., March, 1936.

or wires depend only on the strains. The following discussion is limited to such cases in polycrystalline metals and all phenomena related to creep are here excluded.

Probably, P. Ludwik,[2] working with A. Leon, was one of the first to try to construct the stress-strain curves of tensile, compression, and torsion tests from a common "strain-hardening" curve of the metal. Ludwik used the maximum unit shear and the maximum shearing stress as his variables, following the ideas of O. Mohr[3] and of J. Guest.[4] Two great forward steps were made when H. Hencky[5] and R. v. Mises[6] replaced these two variables by two new ones, namely by two invariants of the strain and of the stress tensor, and when they introduced the elastic energy of distortion in their expression for the condition of plasticity of ductile metals. These conditions in the strain-hardening range have been further treated by F. Koerber,[7] G. Sachs,[8] E. Siebel,[9] A. Eichinger and M. Ros,[10] R. Schmidt,[11] G. Baranski,[12] and others.[13]

Principal Stress and Strain Octahedron

We shall designate the normal stresses by σ and the shearing stresses by τ. The subscripts 1, 2, and 3 will be used to designate the three principal directions of stress, so that the principal stresses are σ_1, σ_2, and σ_3. Consider a point, P, situated at the center of a small cube whose edges are parallel to the principal stress directions. The stress components σ_n and τ_n shall be considered for plane sections perpendicular to the four body diagonals of the cube which latter have direction cosines $\pm 1/\sqrt{3}$ with respect to the principal directions 1, 2, and 3. There are four sets of such planes. They are parallel to the planes of a regular octahedron which can be constructed around the point P as a center. The corners of this principal octahedron of stress are situated on the principal axes of stress at equal distances from the origin, 0. The normal and the shearing stresses σ_n and τ_n for any of the eight planes of the octahedron are called the octahedral normal or octahedral shearing stresses. The stress σ_n is equal to the mean normal stress:

$$\sigma_n = (\sigma_1+\sigma_2+\sigma_3)/3, \tag{1}$$

and the octahedral shearing stress, τ_n, is equal to

$$\tau_n = \tfrac{1}{3}\cdot((\sigma_1-\sigma_2)^2+(\sigma_2-\sigma_3)^2+(\sigma_3-\sigma_1)^2)^{\frac{1}{2}}. \tag{2}$$

The direction, in an octahedral plane, in which the corresponding stress, τ_n, acts can be found easily from Fig. 1.[14]

In ductile metals, the limit at which plastic yielding starts seems to be independent of the mean normal stress, σ_n. The octahedral shearing stress, τ_n, is therefore an essential quantity, and is a variable which defines the various states of stress at which it is possible to have plastic equilibrium. *A substance which yields when the octahedral shearing stress $\tau_n=\tau_0=$ const. is said to be perfectly plastic.*

From Mohr's graphical representation of tensors it is known that *the principal shearing stresses*, τ_1, τ_2, τ_3, act in the planes which bisect the right angles between the principal planes, and that they are equal to

$$\tau_1=\frac{\sigma_2-\sigma_3}{2}, \quad \tau_2=\frac{\sigma_3-\sigma_1}{2}, \quad \tau_3=\frac{\sigma_1-\sigma_2}{2}, \tag{3}$$

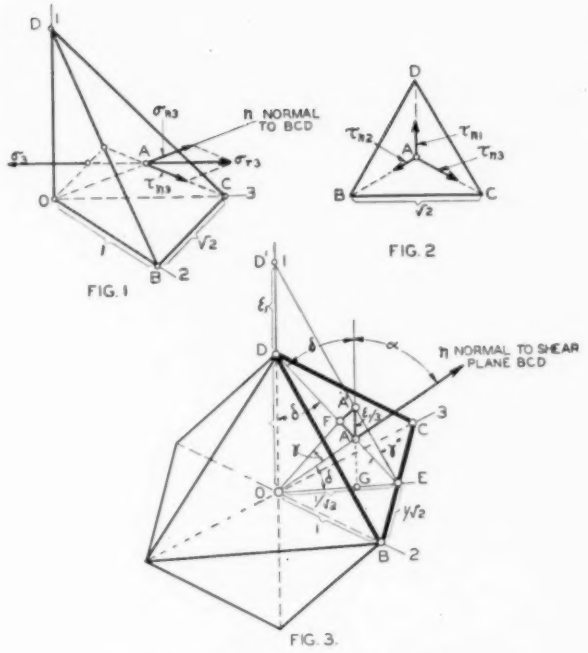
$$\tau_1+\tau_2+\tau_3=0. \tag{4}$$

[2] P. Ludwik, *Elemente der Technologischen Mechanik* (J. Springer, Berlin, 1909).
[3] Abhandlungen, second edition (W. Ernst u. Sohn, Berlin, 1914).
[4] Phil. Mag. (1900).
[5] Various papers.
[6] *Göttinger Nachrichten* (1913).
[7] Mitt. Kaiser Wilhelm Inst. fuer Eisenforschung, Düsseldorf.
[8] *Praktische Metallkunde*, 2 Vol. (J. Springer, Berlin, 1934).
[9] *Die Verformung im bildsamen Zustande* (Stahleisen, Düsseldorf, 1932).
[10] *Versuche zur Klaerung der Frage der Bruchgefahr*, Bericht Nr 34, Eidgenössische Material prüfungs anstalt (Zürich, 1929).
[11] Dissertation, Göttingen, J. Springer, Berlin, 1932.
[12] Zeitschrift fuer Metallkunde **26**, 173 (1934).
[13] Compare also Bulletins No. 115 and 185 of the Experimental Station of the University of Illinois (Reports by F. B. Seely, W. I. Putman, F. E. Richart, A. Brandtzaeg). —The change of the hardness after cold work is the subject of a large number of investigations; another important phase of the problem is concerned with the mechanism of strain hardening in single crystals, which has been discussed by G. I. Taylor, E. Orowan and others.

[14] Eqs. (1) and (2) may be verified by computing the stress components, σ_n and τ_n, in the octahedral plane *BCD* of Fig. 1. Assuming that $\sigma_1=0$, $\sigma_2=0$ and that only σ_3 is acting, this gives $\sigma_{n3}=\sigma_3/3$ and $\tau_{n3}=\sqrt{2}\cdot\sigma_3/3$. Similarly, the three symmetry lines in the equilateral triangle *BCD*, which represents one of the octahedral planes, define the directions of the three coplanar vectors (Fig. 2):

$$\tau_{n1}=\sqrt{2}\cdot\sigma_1/3, \quad \tau_{n2}=\sqrt{2}\cdot\sigma_2/3, \quad \tau_{n3}=\sqrt{2}\cdot\sigma_3/3.$$

Their resultant is τ_n of Eq. (2). (See J. App. Mech. A.S.M.E. **1**, 116 (1933)).



FIGS. 1, 2 AND 3. Principal octahedron.

A second form for τ_n is found after substituting the values from (3) in (2):

$$\tau_n = \tfrac{2}{3} \cdot (\tau_1^2 + \tau_2^2 + \tau_3^2)^{\frac{1}{2}}. \tag{5}$$

A third form for τ_n follows after eliminating one of the principal shearing stresses, for example τ_3, from (4) and (5):

$$\tau_n = \tfrac{2}{3} \cdot (2(\tau_1^2 + \tau_1\tau_2 + \tau_2^2))^{\frac{1}{2}}. \tag{6}$$

When introducing strains we have to distinguish whether they are elastic or permanent (plastic) strains and whether the plastic strains are infinitesimally small or finite.

Infinitesimal Strains

The geometrical properties of a state of infinitesimal strains are identical with those of the state of stress. We shall designate unit extensions by ϵ; unit shears by γ; the principal strains by ϵ_1, ϵ_2, ϵ_3; the principal shears by γ_1, γ_2, γ_3. The normals of the planes of the principal octahedron of strain have the direction cosines $\pm 1/\sqrt{3}$ with respect to the axes of principal strain. The octahedral strain ϵ_n is the unit extension in the directions normal to the planes of the octahedron and equal to the mean strain $(\epsilon_1+\epsilon_2+\epsilon_3)/3$. When the strains are purely plastic, the dilatation of the volume is negligible. For purely plastic strains, therefore, the octahedral strain ϵ_n vanishes, and

$$\epsilon_n = (\epsilon_1+\epsilon_2+\epsilon_3)/3 = 0. \tag{7}$$

The octahedral shear, γ_n, is the unit shear in the planes of the octahedron, and is defined in the form of Eq. (2)[15] as

$$\gamma_n = \tfrac{2}{3} \cdot ((\epsilon_1-\epsilon_2)^2 + (\epsilon_2-\epsilon_3)^2 + (\epsilon_3-\epsilon_1)^2)^{\frac{1}{2}}. \tag{8}$$

An infinitesimal plastic deformation can now be described as follows. Consider as an element of material the principal octahedron, the axes of which coincide with the principal directions of stress or of strain. The plastic distortion consists only of pure shears, of magnitude γ_n, and the extensions normal to the planes of the octahedron vanish. The special tensor for this type of distortion has sometimes been called a "deviator." For the octahedral shear, γ_n, the formula corresponding to Eq. (6) is

$$\gamma_n = \tfrac{2}{3} \cdot (2(\gamma_1^2 + \gamma_1\gamma_2 + \gamma_2^2))^{\frac{1}{2}}. \tag{9}$$

The principal shears which appear here are defined by

$$\gamma_1 = \epsilon_2 - \epsilon_3, \quad \gamma_2 = \epsilon_3 - \epsilon_1, \quad \gamma_3 = \epsilon_1 - \epsilon_2. \tag{10}$$

If (10) is substituted in (9) we have

$$\gamma_n = 2(2(\epsilon_1^2 + \epsilon_1\epsilon_2 + \epsilon_2^2)/3)^{\frac{1}{2}}. \tag{11}$$

The formulae for ϵ_n and γ_n can be obtained directly by showing how much each of the principal strains, ϵ_1, ϵ_2, ϵ_3, contributes to the octahedral strains ϵ_n and γ_n. If, for example, only ϵ_1 exists and $\epsilon_2 = \epsilon_3 = 0$, it is easy to see that the corresponding contributions are

$$\epsilon_{n_1} = \epsilon_1/3, \quad \gamma_{n_1} = 2\sqrt{2} \cdot \epsilon_1/3.$$

Similar contributions are due to the strains ϵ_2 and ϵ_3. The three amounts ϵ_{n_1}, ϵ_{n_2}, ϵ_{n_3}, are added algebraically, while γ_{n_1}, γ_{n_2}, γ_{n_3}, must be added as three coplanar vectors in the same way as is

[15] The factor 2 in Eq. (8) is missing in the corresponding Eq. (2) for stress, because the scheme of correspondence to be followed when the formulae for stress have to be converted into those for strain:

stresses: σ, τ
strains: $\epsilon, \gamma/2$

shown in Fig. 2 for the shearing stress components τ_{n_1}, τ_{n_2}, τ_{n_3}.[16]

Conventional and Natural Strains

In dealing with *finite* strains, we shall consider first the case in which the principal directions do not change in space. Let a, b, and c, be the dimensions of an element in three mutually perpendicular directions which are so chosen that after distortion they coincide with the principal directions of strain. Let a', b', and c', be their lengths after distortion. The conventional unit elongations, or strains, in these directions are defined by

$$\epsilon_1=(a'/a)-1, \quad \epsilon_2=(b'/b)-1, \quad \epsilon_3=(c'/c)-1. \tag{12}$$

For the increments da', db', and dc', these strains will change by the differentials

$$d\epsilon_1=da'/a, \quad d\epsilon_2=db'/b, \quad d\epsilon_3=dc'/c, \tag{13}$$

in which, a, b, and c are constant. P. Ludwik, H. Hencky, and others have remarked that in the case of large deformations it is preferable to define the increments of strain not by Eq. (13), (i.e., by referring them to the arbitrary, "original" lengths a, b, and c), but to divide the differentials da', db', and dc' by the actual lengths of the elements, thus obtaining

$$d\mathfrak{e}_1=da'/a', \quad d\mathfrak{e}_2=db'/b', \quad d\mathfrak{e}_3=dc'/c'. \tag{14}$$

This means that, instead of the *conventional strains* ϵ_1, ϵ_2, ϵ_3, we define new strains $\mathfrak{e}_1$, $\mathfrak{e}_2$, $\mathfrak{e}_3$, such that

$$\left.\begin{aligned} \mathfrak{e}_1&=\int_a^{a'} da'/a'=\ln(a'/a)=\ln(1+\epsilon_1),\\ \mathfrak{e}_2&=\ln(1+\epsilon_2),\\ \mathfrak{e}_3&=\ln(1+\epsilon_3). \end{aligned}\right\} \tag{15}$$

It is suggested that these new quantities be called "natural strains." The constancy of volume in the case of plastic deformations is expressed by

$$a'b'c'=abc=(1+\epsilon_1)(1+\epsilon_2)(1+\epsilon_3)=1. \tag{16}$$

Taking natural logarithms, Eq. (16) becomes

$$\ln(a'/a)+\ln(b'/b)+\ln(c'/c)=\mathfrak{e}_1+\mathfrak{e}_2+\mathfrak{e}_3=0. \tag{17}$$

This brings out the advantage of introducing the natural strains $\mathfrak{e}$. Eq. (7) expressed that the dilatation is zero for infinitesimal strains. Eq. (7) applied strictly only for infinitesimal strains. It becomes more and more incorrect the larger the strains. Eq. (17), on the other hand, remains valid for strains of any magnitude, provided only that they are defined according to Eq. (15).

When dealing with extremely slow motions of a viscous or plastic or plastico-viscous nature such as for example the slow creep of the ductile metals at elevated temperatures, the rates at which strains change with time t become important variables in establishing the conditions of motion and of equilibrium. When the strain is large, we have to distinguish between the *conventional strain rate*

$$u=\partial\epsilon/\partial t \tag{18}$$

and the *natural* or *true strain rate*[17]

[16] Consider a pure extension ϵ_1. The expressions just given for ϵ_{n_1} and γ_{n_1} are found by computing the extension of the straight lines normal to an octahedral plane and the angle by which these formerly perpendicular directions to an octahedral plane have changed due to a simple extention ϵ_1. This has been indicated in Fig. 3 which shows the principal octahedron drawn in its position relative to the principal axes, 1, 2 and 3. Assume $OB=OC=OD=1$. This makes the length of an edge of the octahedron $=\sqrt{2}$ and the height of the equilateral triangle BCD $DE=(3/2)^{\frac{1}{2}}$. Since A lies at the center of this triangle, $AE=1/\sqrt{6}$, and $OA=1/\sqrt{3}$. Now assume that the distortion consists of a simple extension, $=\epsilon_1$, along the vertical axis, and assume further that $\epsilon_2=\epsilon_3=0$. Point D is displaced to D', and $DD'=\epsilon_1$. The point A is displaced to A', and $AA'=\epsilon_1/3$. The length ED becomes, after distortion, ED'. The cosine of the angle between the normal OA to the octahedral plane BCD and OE is

$$\cos\delta=OA/OE=(1/\sqrt{3})/(1/\sqrt{2})=\sqrt{\tfrac{2}{3}}.$$
$$\sin\delta=1/\sqrt{3}.$$

The unit strain ϵ_{n_1} in the direction of the normal OA to the octahedral plane is equal to the elongation $A'F$ of this length divided by the length OA; i.e.,

$$\epsilon_{n_1}=A'F/OA=AA'(\sin\delta)/OA=\epsilon_1/3.$$

To find the unit shear γ_{n_1} we must define two small angles γ' and γ''. These are the angles by which the two perpendicular directions OA and EA have rotated, respectively. The sum of γ' and γ'' is the unit shear γ_{n_1} caused by the strain ϵ_1. Then,

$$\gamma'=AA'\cos\delta/OA=\epsilon_1\cos\delta/\sqrt{3},$$
$$\gamma''=AA'\sin\delta/AE=\sqrt{\tfrac{2}{3}}\cdot\epsilon_1\sin\delta,$$
$$\gamma_{n_1}=\gamma'+\gamma''=\epsilon_1[(\cos\delta/\sqrt{3})+(\sqrt{\tfrac{2}{3}})\sin\delta]=2\sqrt{2}\cdot\epsilon_1/3.$$

Similar expressions may be found for the shears caused by the strains ϵ_2 and ϵ_3.

[17] If one end or head of a test bar subjected to tension is fixed and the other head is moved by a screw-driven mechanism at a uniform speed, the test bar stretches under the condition $u=$const., while the true strain rate u decreases. To realize a test condition in which $u=$const. (i.e., a constant true strain velocity), it is necessary to increase the relative speed between the heads of the test bar in the same proportion that the length of the bar increases.

$$\mathbf{u}=\partial\boldsymbol{\varepsilon}/\partial t=(\partial/\partial t)\ln(1+\epsilon)$$
$$=(\partial\epsilon/\partial t)/(1+\epsilon)=u/(1+\epsilon). \quad (19)$$

Similarly we must distinguish between a conventional shear, γ, and a natural shear, $\boldsymbol{\gamma}$. A conventional shear γ is measured by the tangent of an angle α

$$\gamma=\tan\alpha. \quad (20)$$

α designates the finite angle by which two planes, which originally were perpendicular to each other, have rotated relatively to each other around their line of intersection. Introducing again the natural strains $\boldsymbol{\varepsilon}_1$, $\boldsymbol{\varepsilon}_2$, $\boldsymbol{\varepsilon}_3$, the natural principal shears are defined by

$$\left.\begin{aligned}\boldsymbol{\gamma}_1&=\boldsymbol{\varepsilon}_2-\boldsymbol{\varepsilon}_3=\ln(1+\epsilon_2)-\ln(1+\epsilon_3),\\ \boldsymbol{\gamma}_2&=\boldsymbol{\varepsilon}_3-\boldsymbol{\varepsilon}_1=\ln(1+\epsilon_3)-\ln(1+\epsilon_1),\\ \boldsymbol{\gamma}_3&=\boldsymbol{\varepsilon}_1-\boldsymbol{\varepsilon}_2=\ln(1+\epsilon_1)-\ln(1+\epsilon_2).\end{aligned}\right\} \quad (21)$$

They satisfy the condition

$$\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2+\boldsymbol{\gamma}_3=0. \quad (22)$$

The natural octahedral shear $\boldsymbol{\gamma}_n$ is defined by the increment $d\boldsymbol{\gamma}_n$ the expression of which is assumed according to Eq. (8):

$$d\boldsymbol{\gamma}_n=\tfrac{2}{3}\cdot((d\boldsymbol{\varepsilon}_1-d\boldsymbol{\varepsilon}_2)^2+\cdots)^{\frac{1}{2}}, \quad (23)$$

which expression after using Eq. (17) can be simplified to

$$d\boldsymbol{\gamma}_n=2(2(d\boldsymbol{\varepsilon}_1^2+d\boldsymbol{\varepsilon}_1\cdot d\boldsymbol{\varepsilon}_2+d\boldsymbol{\varepsilon}_2^2)/3)^{\frac{1}{2}}. \quad (24)$$

By substituting the principal shears from

$$d\boldsymbol{\gamma}_1=d\boldsymbol{\varepsilon}_2-d\boldsymbol{\varepsilon}_3,\ \cdots \quad (25)$$

in (24) a third expression is found for $d\boldsymbol{\gamma}_n$:

$$d\boldsymbol{\gamma}_n=\tfrac{2}{3}\cdot(2\cdot(d\boldsymbol{\gamma}_1^2+d\boldsymbol{\gamma}_1\cdot d\boldsymbol{\gamma}_2+d\boldsymbol{\gamma}_2^2))^{\frac{1}{2}}. \quad (26)$$

The physical meaning of these three formulae (Eqs. 23–26) is this: assume that a cubical element of material is distorted plastically so that the directions of the principal strains remain always parallel to the edges of the cube. The increment of shear $d\boldsymbol{\gamma}_n$ expresses the distortion of a regular octahedron assumed in the material in every intermediate state of the distortion. The increments $d\boldsymbol{\gamma}_n$ are referred to the intermediate states and to the instantaneous dimensions of the element of material similarly as the increments of the natural strain $d\boldsymbol{\varepsilon}$ express the changes of lengths per unit length of a prismatic element of material.

When the material is deformed plastically, in many cases the distortion proceeds in a simple manner which is characterized by a condition of the form

$$d\boldsymbol{\varepsilon}_2=k\cdot d\boldsymbol{\varepsilon}_1, \quad (27)$$

where k is a given positive or negative constant. In such a case

$$\boldsymbol{\varepsilon}_2=k\cdot\boldsymbol{\varepsilon}_1+c.$$

When the deformation starts from the undistorted state, we have $c=0$; otherwise c expresses the initial plastic distortion. Assuming $c=0$ we see that

$$k=d\boldsymbol{\varepsilon}_2:d\boldsymbol{\varepsilon}_1=\boldsymbol{\varepsilon}_2:\boldsymbol{\varepsilon}_1. \quad (28)$$

Eq. (24) can be integrated and one can define $\boldsymbol{\gamma}_n$ in finite form as:

$$\boldsymbol{\gamma}_n=2\boldsymbol{\varepsilon}_1\cdot(2(1+k+k^2)/3)^{\frac{1}{2}}, \quad (29)$$

or after replacing here k by $\boldsymbol{\varepsilon}_2:\boldsymbol{\varepsilon}_1$ also as

$$\boldsymbol{\gamma}_n=2(2(\boldsymbol{\varepsilon}_1^2+\boldsymbol{\varepsilon}_1\boldsymbol{\varepsilon}_2+\boldsymbol{\varepsilon}_2^2)/3)^{\frac{1}{2}}. \quad (30)$$

In the strain-hardening range of the ductile deformations, the yield stresses in the metals increase considerably with the strains. Since yielding does not seem to depend on the *mean normal stress*, one can express strain-hardening by assuming that the octahedral shearing stress τ_n is dependent on the octahedral shear $\boldsymbol{\gamma}_n$:

$$\tau_n=f(\boldsymbol{\gamma}_n). \quad (31)$$

If such a relation were valid in the strain-hardening range of the deformation, one could predict from this function the shapes of the various "stress-strain curves" corresponding to special types of strains, such as for example the stress-strain curve obtained from a tensile, compression or torsion test.

The preceding analysis of finite plastic strains assumed (1) that the elastic portions of the strains were small and could therefore entirely be neglected and (2) that the principal directions of stress coincided with the principal directions of strain and of strainrate. In certain special cases (for example when the residual stresses after severe cold work have to be computed) it is necessary to consider the elastic strains although they may be small. It is furthermore important to note in general cases of plastic flow that (3) the principal directions of strain rotate both absolutely with reference to fixed coordinate

axes in space as well as also relatively to the deforming material itself, and that (4) when the stress tensor is not coaxial with the plastic strain tensor the former tends to drag the latter into its own direction. Since the conditions 1, 3 and 4 make the treatment considerably more difficult and the conditions 3 and 4 are becoming only important for large strains, all that can be said here is that the simple analysis described in the examples below, in which rotations occur, should be applied for strains which are not too large.

Strain-Hardening Curve for Tension or Compression

Taking the principal stress σ_1 in the direction of tension, we have for a tensile test $\sigma_2=\sigma_3=0$ and $\epsilon_2=\epsilon_3=-\epsilon_1/2$. Let l_0 be the original length and A_0 the original cross-sectional area of the bar, and l and A the length and cross-sectional area after the bar has been stretched, then

$$\ln\,(l/l_0)=\ln\,(A_0/A)=\ln\,(1+\epsilon_1)=\epsilon_1$$

The "true" stress σ is the load P divided by the area A

$$\sigma=P/A=P\cdot(1+\epsilon_1)/A_0=\sigma\cdot(1+\epsilon_1). \quad (32)$$

It is necessary to distinguish the true stress σ from the loadstress $\sigma=P/A_0$, which is the load P divided by the original area A_0.

The octahedral shearing stress τ_n (see Eq. (2)) is:

$$\tau_n=\sqrt{2}\cdot\sigma/3=\sqrt{2}\cdot\sigma\cdot(1+\epsilon_1)/3, \quad (33)$$

and the corresponding shear γ, is (this is a special case of Eq. (29) in which $k=-1/2$)

$$\gamma_n=\sqrt{2}\cdot\epsilon_1=\sqrt{2}\cdot\ln\,(1+\epsilon_1). \quad (34)$$

These last two equations allow to construct the strain hardening curve $\tau_n=f(\gamma_n)$ of the material

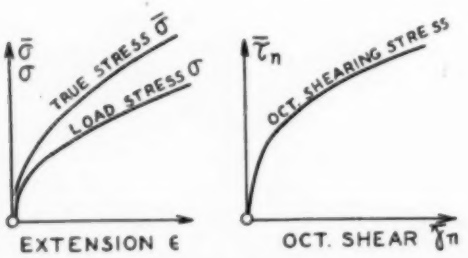


FIG. 4. Conventional tensile stress-strain diagram (left) and strain-hardening curve (right). (Letters with bars are used in place of the bold faced letters in text.)

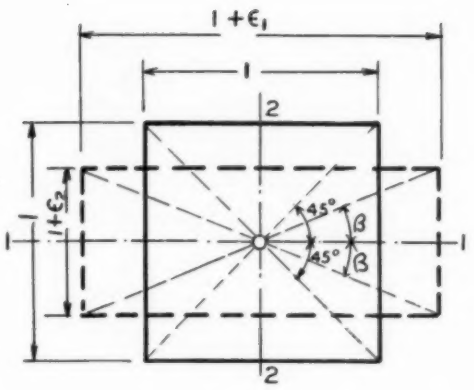


FIG. 5.

from the observed conventional stress strain curve $\sigma=f_1(\epsilon_1)$ of a tensile test (Fig. 4).

Strain-Hardening Curve for Shear

(*a*) *Pure shear.*—We have

$$(1+\epsilon_1)(1+\epsilon_2)=1, \quad \epsilon_3=0. \quad (35)$$

Since ϵ_3 is zero, we have:

$$\epsilon_2=-\epsilon_1 \quad (36)$$

and according to Eq. (29) $\epsilon_2/\epsilon_1=k=-1$, so that

$$\gamma_n=2(\tfrac{2}{3})^{\frac{1}{2}}\cdot\epsilon_1. \quad (37)$$

The conventional unit shear γ which measures this distorsion is (see Fig. 5)

$$\gamma=\tan\,[(\pi/2)-2\beta]=\tfrac{1}{2}(\cot\,\beta-\tan\,\beta). \quad (38)$$

Since

$$\tan\,\beta=(1+\epsilon_2)/(1+\epsilon_1)=1/(1+\epsilon_1)^2$$

$$\ln\,\tan\,\beta=-2\,\ln\,(1+\epsilon_1)=-2\epsilon_1 \quad (39)$$

therefore

$$\gamma=\sinh\,2\epsilon_1. \quad (40)$$

By combining Eqs. (37) and (40) we obtain the relation which converts the conventional shear γ into the shear γ

$$\gamma=(\tfrac{2}{3})^{\frac{1}{2}}\cdot\sinh^{-1}\,\gamma=(\tfrac{2}{3})^{\frac{1}{2}}\cdot\ln\,[\gamma+(1+\gamma^2)^{\frac{1}{2}}]. \quad (41)$$

When a wide metal sheet is rolled, this type of distorsion occurs. The reduction of thickness q is $(h_0-h):h_0=-\epsilon_2$. Therefore, when a metal sheet is rolled, we have:

$$\ln\,(h/h_0)=\ln\,(1+\epsilon_2)=\ln\,(1-q)=\epsilon_2=-\epsilon_1$$

$$\gamma_n=2(\tfrac{2}{3})^{\frac{1}{2}}\cdot\ln\,h_0/h$$

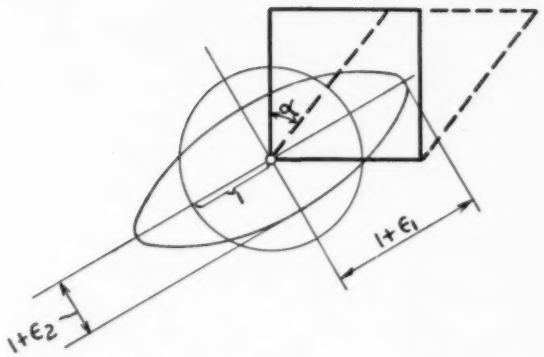


FIG. 6.

or finally:

$$\gamma_n = -2(\tfrac{2}{3})^{\frac{1}{2}} \cdot \ln\,(1-q). \qquad (42)$$

This last formula expresses the octahedral shear γ_n for large reductions of thickness q.

(*b*) *Simple shear. (Torsion problem.)*—A circle drawn in the plane of shear having the radius of unity is distorted by shear into an ellipse with the semi-axes $1+\epsilon_1$ and $1+\epsilon_2$. The third principal strain ϵ_3 is zero. If the squares of the semi-axes are designated by λ_1 and λ_2, these in terms of the conventional shear (see Fig. 6) are expressed by the formulae:

$$\left.\begin{aligned} \lambda_1 &= (1+\epsilon_1)^2 = 1+(\gamma^2/2)+\gamma(1+\gamma^2/4)^{\frac{1}{2}}, \\ \lambda_2 &= (1+\epsilon_2)^2 = 1+(\gamma^2/2)-\gamma(1+\gamma^2/4)^{\frac{1}{2}}. \end{aligned}\right\} \qquad (43)$$

The natural strains for a simple shear are therefore:

$$\left.\begin{aligned} \varepsilon_1 &= \ln\,(1+\epsilon_1) = \tfrac{1}{2}\cdot\ln\,\lambda_1, \\ \varepsilon_2 &= \ln\,(1+\epsilon_2) = \tfrac{1}{2}\cdot\ln\,\lambda_2. \end{aligned}\right\} \qquad (44)$$

Since $\varepsilon_3 = 0$ we have here

$$\varepsilon_1 = -\varepsilon_2, \quad \ln\lambda_1 + \ln\lambda_2 = 0, \quad \lambda_1\lambda_2 = 1. \qquad (45)$$

The constant k in Eq. (27) is here again -1, and

$$\gamma_n = 2(2(\varepsilon_1^2+\varepsilon_1\cdot\varepsilon_2+\varepsilon_2^2)/3)^{\frac{1}{2}} \qquad (46)$$

becomes $\gamma_n = (\tfrac{2}{3})^{\frac{1}{2}}\cdot\ln\lambda_1$

$$\gamma_n = (\tfrac{2}{3})^{\frac{1}{2}}\cdot\ln\left[1+\frac{\gamma^2}{2}+\gamma\left(1+\frac{\gamma^2}{4}\right)^{\frac{1}{2}}\right], \qquad (47)$$

which expresses the octahedral shear γ_n in terms of the conventional shear γ. Eq. (47) is needed when the strain hardening curve: $\tau_n = f(\gamma_n)$ of a metal is to be constructed from the experimental results of a torsion test made with a cylindrical bar. From observation the torque M is given as a function of the angle of twist ϕ. From the angle of twist ϕ the conventional maximum unit shear γ in the circular cross sections is obtained by

$$\gamma = a\phi/l, \qquad (48)$$

where a is the radius of cross section and l is the length of the bar.

The Stress-Strain Curves of a Cold Worked Metal Constructed from the Curve of the Annealed Metal

The virgin curve for the load stress, $\sigma = f(\epsilon)$ as a function of the conventional strain, ϵ, is shown for a tensile test in the lowest curve, $OA_1A_2\cdots A_m$ in Fig. 7. Only the portion of this curve below the maximum load marked by the point A_m has been traced. The dotted curve $OB_1B_2\cdots B_m$ is the corresponding true stress curve $\boldsymbol{\sigma} = \sigma\cdot(1+\epsilon)$. The stress in A_m is designated by σ_m and in B_m by $\boldsymbol{\sigma}_m$ and the common abscissa of these points is ϵ_m. σ_m is the engineers' "tensile strength" of the metal corresponding to a fully annealed initial condition. A little consideration enables us to predict the new shapes of the stress-strain curves of the metal after it has been strain-hardened through cold work in tensile tests. The load stress curves of the cold worked metal are indicated by the letters σ_1, σ_2, $\sigma_3\cdots$ for various amounts of prestretching $\epsilon_0 = 5$, 10,

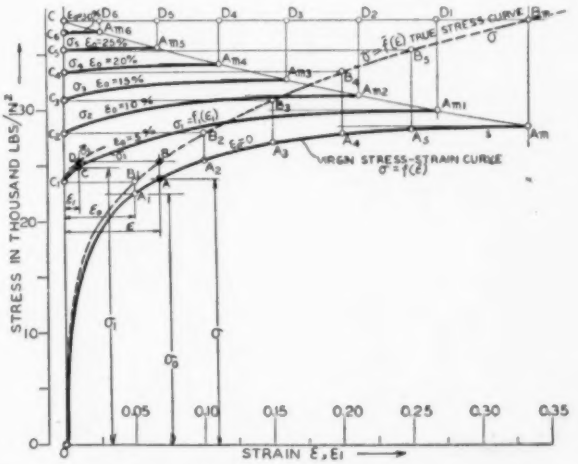


FIG. 7. Stress-strain curves of a cold worked metal constructed from the curve for the annealed metal.

15 percent ··· (see Fig. 7). Let us assume that the metal is first stretched until the strain reaches the value ϵ_0 and the stress the value σ_0, corresponding to a point A_1 on the virgin curve, i.e. ϵ_0, σ_0 express the amount of previous cold work up to the time the test is interrupted. If now a new tensile test is started with the bar, it must be remembered that the new conventional strains ϵ_1 in the second test must be referred to an initial length, which is measured on the bar having already been stretched to point A_1 and to the strain ϵ_0. The initial point C_1 of the new stress-strain curve, $\sigma_1=f_1(\epsilon_1)$, is found by projecting the point B_1 of the true stress curve, $\boldsymbol{\sigma}$, on the ordinate axis.

Let l and l_1 be the lengths of the bar corresponding to the states of strain represented by the points A and A_1, respectively, on the virgin curve and let l_0 be the original bar length. Then, the strains ϵ and ϵ_0 are:

$$\epsilon=(l-l_0)/l_0, \quad \epsilon_0=(l_1-l_0)/l_0 \tag{49}$$

the new strain ϵ_1 is

$$\epsilon_1=(l-l_1)/l_1=\frac{l}{l_0}\cdot\frac{l_0}{l_1}-1=\frac{1+\epsilon}{1+\epsilon_0}-1, \tag{50}$$

the new load stress σ_1, is found from the condition $\boldsymbol{\sigma}_1=\boldsymbol{\sigma}$ or

$$\sigma_1(1+\epsilon_1)=\sigma(1+\epsilon). \tag{51}$$

When the metal is strain-hardened to the initial strain, ϵ_0, the shape of the new stress-strain curve $\sigma_1=f_1(\epsilon_1)$ (curve C_1CA_{m1}) is determined through the shapes of the two virgin curves $\sigma=f(\epsilon)$ and $\boldsymbol{\sigma}=\mathbf{f}(\boldsymbol{\epsilon})$. In terms of ϵ_0 and of the old variables, ϵ, σ the new strain ϵ_1 and the new stress σ_1 is expressed by:

$$\begin{aligned} &\text{new strain} && \epsilon_1=(\epsilon-\epsilon_0)/(1+\epsilon_0) \\ &\text{new stress} && \sigma_1=(1+\epsilon_0)\sigma. \end{aligned} \tag{52}$$

A set of such stress-strain curves is shown in Fig. 7 for the various degrees of cold working ($\epsilon_0=5$, 10, ··· percent). By eliminating ϵ_0 from the last two equations one obtains

$$\sigma_1=[(1+\epsilon)/(1+\epsilon_1)]\cdot\sigma, \tag{53}$$

which is the same as Eq. (51). When σ_1 and ϵ_1 are interpreted as rectangular coordinates and ϵ as a parameter this is the family of the curves

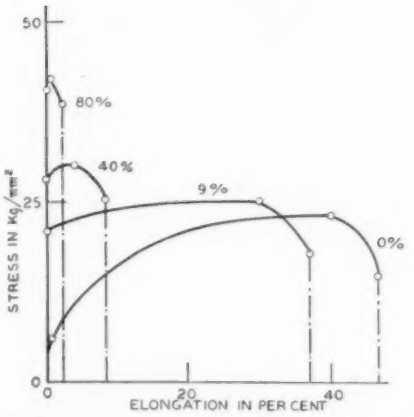


FIG. 8. Tensile diagrams for copper which has been cold-rolled to 9, 40 and 80 percent reduction; according to H. O'Neill and T. W. Cuthbertson.

for constant amount of strain hardening. Thus, we see that the family of curves connecting the points in the various stress-strain curves $\sigma_1=f_1(\epsilon_1)$ having the same cold work is a family of equilateral hyperbolas. Consequently, the maximum load-stresses σ_{1m} of the various stress-strain curves (i.e., the "tensile strengths" for various degrees of coldwork) must also satisfy the hyperbola:

$$\sigma_{1m}=[(1+\epsilon_m)/(1+\epsilon_{1m})]\cdot\sigma_m. \tag{54}$$

in function of the strains ϵ_{1m}. ϵ_m and σ_m are here the coordinates of the point A_m of the virgin curve, ϵ_m is the strain and σ_m the stress at the ultimate strength of the annealed metal. This limiting hyperbola is the curve $A_mA_{m1}A_{m2}$ ··· in Fig. 7.

The family of curves Fig. 7 brings out the well-known fact that the more a metal has been hardened through stretching, the shorter the stress-strain curves become. It would thus appear from Fig. 7 that it would not be possible to strain-harden a metal through uniform stretching under a tensile stress *above the true stress* $\boldsymbol{\sigma}_m$ at the load maximum σ_m of the annealed metal (point B_m). This seems a reasonable conclusion. What occurs in the metal *after necking starts* has not been considered here and cannot be considered without introducing here an entirely new question concerning the effect of the speed of deformation or of stretching which influences the mode of necking.

It may be of interest to compare some of the conclusions with tests. A set of tensile diagrams

TABLE I. *Tensile properties of cold drawn copper according to Alkins.*

Wire Diameter d Inch	Reduction of Area q %	Corresponding Axial Strain $1+\epsilon_0 = 1/(1-q)$	Observed Tensile Strength σ_{m1} lb./in.²	Computed Tensile Strength According to Eq. 52 $\sigma_{m1}=(1+\epsilon_0)\sigma_m$ lb./in.²	Difference of Last Two Columns %
0.4342	——	1	30200	30200	—
0.4305	1.63	1.016	30700	30700	0
0.4250	4.19	1.044	31600	31500	0.3
0.4195	6.66	1.072	32500	32400	0.3
0.4150	8.65	1.095	33000	33100	−0.3
0.4094	11.10	1.125	34000	34000	0
0.4052	12.89	1.148	34200	34700	−1.5
0.4001	15.09	1.178	35400	35600	−0.6
0.3947	17.36	1.211	36800	36600	0.5
0.3898	19.40	1.241	38400	37500	2.3
0.3853	21.25	1.271	39800	38400	3.5
0.3796	23.61	1.309	40100	39500	1.5
0.3752	25.33	1.339	41400	40400	2.4
0.3706	27.15	1.374	42300	41500	1.9
0.3651	29.30	1.414	43100	42700	0.9
0.3602	31.18	1.453	44000	43900	
0.3552	33.08	1.495	44500	45100	
0.3497	35.13	1.543	44600	46600	formula
0.3454	36.72	1.580	45200	47700	is invalid
0.3397	38.78	1.634	46700	49900	
0.3353	40.36	1.681	46200	50900	

similar to the ones just discussed has been observed in cold rolled copper by H. O'Neill and T. W. Cuthbertson.[18] It is well known that through cold rolling or cold drawing much higher degrees of cold work can be produced, than by simple tension without lateral compression.

The trend of the observed stress-strain curves of copper reproduced in Fig. 8 is merely shown as an illustration of the conditions discussed in Fig. 7.

Some experiments reported by W. E. Alkins[19] on properties of cold drawn copper wires can be utilized for a closer comparison. Alkins cold worked copper by drawing through dies from 0.434 inch diameter to 0.296 inch. After each pass the tensile strength was determined in tension tests. Table I reproduces some of his observations. The values of the tensile strengths found by Alkins are given in the fourth column; the fifth column shows the values of the tensile strengths computed from Eq. (54) using for $\sigma_m = 30200$ lb./in.² and taking $1+\epsilon_0 = 1:(1-q)$ where q is the reduction of area given by Alkins. The agreement between the observed and computed values of σ_{m1} is almost perfect at lower amounts of cold work and is still good up to the region of $\epsilon_0 = \epsilon_m = 40$ percent corresponding approximately to cold working the metal to the tensile strength of $\sigma_m = 30{,}000$ lb./in.². When $\epsilon_0 > \epsilon_m$ our Eq. (54) becomes invalid.

[18] J. Inst. Metals **46**, 273 (1931).

[19] J. Inst. Metals **46**, 304 (1931).

Plastic Behavior of Metals in the Strain-Hardening Range. Part II

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In order to observe the behavior of a material under various conditions of strain-hardening, copper bars were tested in tension, in compression and in torsion. The results of the different tests were plotted on the same set of coordinates as a means of correlation. The shearing stress in the octahedral planes was used as ordinates and the corresponding octahedral shearing strain was used as abscissae. Good agreement was found between the curves for tension, compression, and torsion for small strains, but for very large strains (as obtained near the ultimate strength of annealed copper) the curves tend to separate to a marked degree. Hardness readings were also taken to check the relation between hardness and strain.

THE theory of the plastic behavior of metals in the strain-hardening range has been treated by A. Nadai[1] in a previous article. Other investigations which lie close to the scope of the present paper have been carried out by P. Ludwik and R. Scheu,[2] M. Ros and A.

[1] A. Nadai, "Plastic Behavior of Metals in the Strain-Hardening Range," J. App. Phys. this issue.

[2] P. Ludwik and R. Scheu, "Vergleichende Zug-Druck-, Dreh- und Walzversucke," Stahl und Eisen **45**, 373 (1925).

Eichinger,[3] E. Siebel,[4] R. Schmidt,[5] and G. Baranski.[6]

Ludwik and Scheu made comparative tension, compression and torsion tests with round copper bars. They plotted the maximum shearing stress τ_{max} as a function of the maximum unit shears γ_{max} and found that for small values of γ_{max} the stress-strain curve $\tau_{max}=f(\gamma_{max})$ from the torsion tests had larger ordinates than the corresponding curve from the tension tests. For large values of γ_{max} they found that the ordinates of the curve for tension were the larger.

Ros and Eichinger investigated the behavior of hollow cylinders subjected to various combinations of internal pressure, axial tension or compression, and torsion. They plotted the curves $\tau_{max}=f(\gamma_{max})$, $\sigma_{max}=f(\epsilon_{max})$ and $\tau_n=f(\gamma_n)$ where σ and ϵ represent tensile stress and strain and τ_n and γ_n represent the shearing stress and strain in the octahedral planes as described by Nadai.[1]

Schmidt used a special tension-torsion machine designed in 1925 by Nadai[7] for tests under combined stress. The test specimens, which were tubes of mild steel and of copper, were tested simultaneously in tension and in torsion in such a manner that the ratio $\epsilon : \gamma$ remained constant during the test. Schmidt's results on copper are shown in Fig. 1.

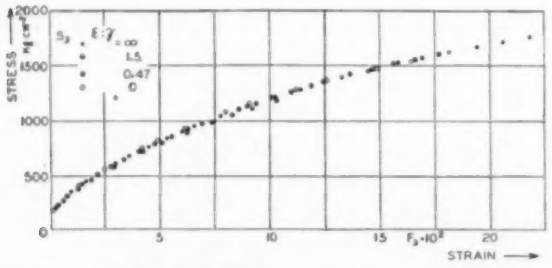

FIG. 1. Schmidt's data on tension-torsion tests on copper. The abscissa are proportional to $\gamma_n=\frac{2}{3}((\epsilon_1-\epsilon_2)^2+\cdots)^{\frac{1}{2}}$. The ordinate are proportional to $\tau_n=\frac{1}{3}((\sigma_1-\sigma_2)^2+\cdots)^{\frac{1}{2}}$ γ_n is the octahedral shearing strain. τ_n is the octahedral shearing stress.

[3] M. Ros and A. Eichinger, "Versuche Zur Klaerung der Frage der Bruchgefahr," Bericht Nr. 34, Eidgenoessische Material Pruefungsanstalt, Zurich, 1929.

[4] E. Siebel, *Die Verformung im bildsamen Zustande* (Stahleisen, Duesseldorf, 1932).

[5] R. Schmidt, *Dissertation, Goettingen* (J. Springer, Berlin, 1932).

[6] G. Baranski, "Zerreissversuche bei ebener plastischer Verformung," Zeits. f. Metallkunde **26**, 173 (1934).

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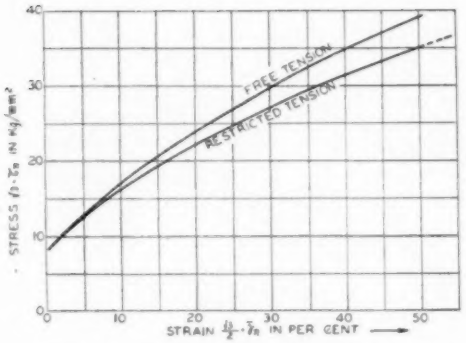

FIG. 2. Strain-hardening curves for brass. (According to Baranski.) (Letter with bar is used in place of bold face in the text.)

The points corresponding to given ratios of axial tensile strain ϵ to torsional shear strain γ follow a common curve quite well.

Baranski made tension tests with flat bars which were tested in such a way that the bars were restricted from contracting laterally in width, but were permitted to contract freely in thickness. He could thus compare the yielding of bars in free tension ($\sigma_2=\sigma_3=0$) and in restricted tension ($\sigma_2=(\sigma_1/2),\sigma_3=0$). His results for brass are shown in Fig. 2. It is interesting to note that the strain-hardening curve for free tension is slightly higher than the corresponding curve for restricted tension. This last type of stress corresponds to the case of pure shear.

In order to observe the behavior of copper under various conditions of strain hardening, tension, compression and torsion tests were made. In addition, the hardness of the copper was observed after the cold working. The material was commercial copper of a purity of 99.9 percent Cu and was annealed at 650°C for approximately one-half hour.

The tension tests were made on a copper strip of $1\frac{1}{4}''\times\frac{1}{4}''$, 20″ long. The bar was elongated in steps and the Vickers hardness was measured after each loading. After the ultimate load was reached the area at the smallest cross section in the neck was observed and used to compute the elongation in the axial direction at this minimum cross section. Vickers hardnesses were also measured in the necked portion. In this way the range of strains was extended to about 100 percent and approximate values of stress and strain beyond the ultimate strength were observed. For the Vickers hardness of the un-

TABLE I. *Copper compression tests.*

Stress σ lb./in.^{2}	ϵ Strain	Vickers Hardness	Stress τ_n lb./in.^{2}	γ_n Shear
8770	0.0154	50	4190	0.0215
14630	0.0407	59	6920	0.0565
20150	0.0690	69	9530	0.0943
25250	0.1015	72	11940	0.1368
32400	0.1615	82	15320	0.212

stressed strip, the low figure of 40 was obtained showing that the copper was in a perfectly soft condition. The bars were not machined where the hardness readings were taken.

Five compression tests were made with copper cylinders of 1 inch diameter and 2.5 inch height, compressed between hardened steel plates in a 200 ton Amsler press using approximately the same velocity of strain in each test. The observed values are given in Table I.

For the torsion tests round bars of $1\frac{1}{8}$ inch diameter with a gauge length of 14 inches were used which were machined out from bars with $1\frac{1}{4}''$ square cross section. The tests were made in a 1200 ft. lb. Amsler torsion machine with electric drive rotating the moving head with a uniform angular velocity. The torque M and angle of twist ϕ per inch length was measured. The maximum shearing stress τ in the circular cross section was computed from the formula

$$\tau = (1/2\pi a^3)(\phi\, dM/d\phi + 3M), \qquad (1)$$

where a is the radius of the bar. The conventional unit shear was computed from

$$\gamma = a\phi. \qquad (2)$$

After the test bars had been twisted to various amounts they were cut in pieces and the Vickers hardness was observed along the diameter of the circular cross sections. Hardness readings were taken as soon as was feasible after twisting so that the undesired effects of aging or softening were eliminated as far as possible. The hardness and the shearing stress, τ, were then plotted as ordinates above the unit shears γ as abscissae.

Fig. 3 shows for the torsion tests the distribution of hardness found along a radius of the circular cross section as a function of the distance from the center. Four such curves are shown in Fig. 3 for bars Nos. 1, 2 and 3 obtained after different amounts of cold working by twisting. For bar No. 1 two hardness curves are given, the upper was taken using a load of 10 kg and the lower one using a load of 50 kg in the hardness tester. This indicates a slight skin effect due to the machining of the plane cross sections. This was observed also in other cases.†

When a straight circular metal cylinder is twisted permanently around its axis, there should be no cold working of the metal observable in a small region near the axis of the cylinder. Theoretically, the hardness at the center of the circular cross sections of a torsion bar should be the same as in the fully annealed metal (approximately Vickers hardness number 40 in the case of soft copper). From Fig. 3 it follows that this was not the case and the metal was harder at the center of the circular cross section than the fully annealed metal. The skin effect can scarcely account for this increase of hardness in the central region of the cross sections. Nor does it seem probable that it was due to an inaccuracy

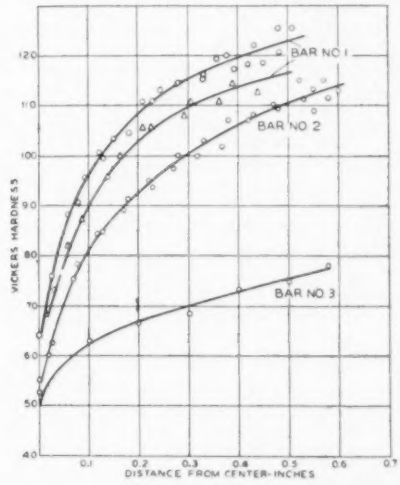

FIG. 3. Torsion tests with cylindrical bars. The distribution of hardness over the cross section after twisting. ○—hardness measured by 10 or 20 kg load. Δ—hardness measured by 50 kg load.

† The effect of surface hardening through machining is further indicated by some observations made on two of the compression cylinders. Both cylinders were first annealed and then machined. On cylinder No. 1 hardness readings were taken after machining while cylinder No. 2 was annealed a second time after the machining.

Load under which indentation is made in kg:		10	20	30	50
Vickers hardness number:	Cylinder No. 1	49	45.5	45.5	42.1
	Cylinder No. 2	44.5	42.8	42.0	41.2

Hardness readings for cylinder No. 2 are lower than for cylinder No. 1 and also lower for larger than for smaller loads both indicating that machining hardens the surface. The lowest hardness values were found in drawn material which had not been machined after it had been annealed.

of locating the small central region of soft material which could have been missed when making the Vickers indentations in the neighborhood of the center of the cross sections. It must be noted that in some of these torsion tests the cold working of the outer portion of the cylinders was extraordinarily strong at the end of the torsion tests. For example, bar No. 1 (radius a =0.563 inch, gauge length 14 inch) was twisted around several times, the test ending with an angle of twist of 5.40 per inch length and with a corresponding maximum shear of $\gamma = 3.04$). It is believed that the observed hardness curves have disclosed an interesting fact which probably has escaped notice in former torsion experiments. It is the permanent volume increase of a severely cold worked metal, which gradually disturbs the simple torsional distribution of stress. It is known that after severe cold work the volume of a metal increases permanently by a very small amount. If the large shears in the outer portions of a long cylinder which has been twisted severely are accompanied by a small permanent increase of volume, the length of the cylinder and probably also its radius must change by a very small amount. As the cross sections of a long cylinder remain plane, the axial strains in the outer portions will have the effect of permanently straining also the inner and central portions of the cylinder in the axial and in radial directions. In other words, permanent volume changes must create a secondary radial-symmetrical strain field which combines with the simple distribution of shears ordinarily assumed to form the true stress distribution of a severely twisted round bar.

An attempt was made to compare the results of the tension, compression, torsion and hardness tests of copper. For the independent variable to express the amount of strain hardening the octahedral shear γ_n was chosen. In the case of tension or compression corresponding to a strain ϵ, γ_n was taken as

$$\gamma_n = \sqrt{2}\,\ln\,(1+\epsilon) \qquad (3)^*$$

while in the torsion test γ_n is given by

$$\gamma_n = \sqrt{\frac{2}{3}}\ln\left(1+\frac{\gamma^2}{2}+\gamma\left(1+\frac{\gamma^2}{4}\right)^{\frac{1}{2}}\right). \qquad (4)$$

TABLE II. *Tension test with copper.*

Conventional Strain ϵ	True Tensile Stress σ lb./in.^{2}	Natural Strain $\mathfrak{E}$	Octahedral Shear γ_n	Octahedral Shearing Stress τ_n lb./in.^{2}	Vickers Hardness
0.02	9500	0.0198	0.028	4460	52
0.04	13800	0.0392	0.056	6480	59
0.06	17400	0.0583	0.082	8170	65
0.1	22900	0.0953	0.135	10750	73
0.2	32000	0.1823	0.258	15050	86
0.3	36800	0.2624	0.371	17300	92
0.4	40500	0.3365	0.476	19020	97
0.5	43500	0.4054	0.573	20450	100
0.6	46000	0.4700	0.665	21600	103
0.7	48200	0.5306	0.751	22650	105

TABLE III. *Torsion test, copper bar No. 1.*

Shear γ	Shearing Stress τ lb./in.^{2}	γ_n	τ_n lb./in.^{2}	Vickers Hardness
0.05	7800	0.0406	6380	68
0.10	10700	0.082	8750	72
0.20	14200	0.163	11600	79
0.30	16700	0.244	13650	86
0.40	18300	0.323	15000	91
0.50	19300	0.404	15800	96
0.60	20200	0.484	16500	99
0.70	20800	0.560	17000	102
0.90	21500	0.712	17600	106

As dependent variables either the Vickers hardness numbers or the true shearing stresses τ_n in the instantaneous octahedral planes were used. For the tension test τ_n is given as

$$\tau_n = \frac{\sqrt{2}}{3}\sigma, \qquad (5)$$

where σ is the true tensile stress. For the torsion test τ_n is given as

$$\tau_n = (\tfrac{2}{3})^{\frac{1}{2}}\tau = 0.817\tau, \qquad (6)$$

where τ is the maximum shearing stress acting at the periphery of the circular cross sections of the torsion bar as computed from Eq. (1). A few values are given in Tables II and III.

Fig. 4 shows the hardness values obtained in tension, compression and torsion tests with the increasing amount of cold work designated by the shearing strain γ_n plotted as the abscissa. With exception of the region of small strains, where the discrepancies already mentioned reappear, the points belonging to five different hardness curves are distributed within a fairly narrow strip. A closer agreement between

* Eqs. (3), (4), (5) and (6) are the equations developed by Nadai in reference No. 1.

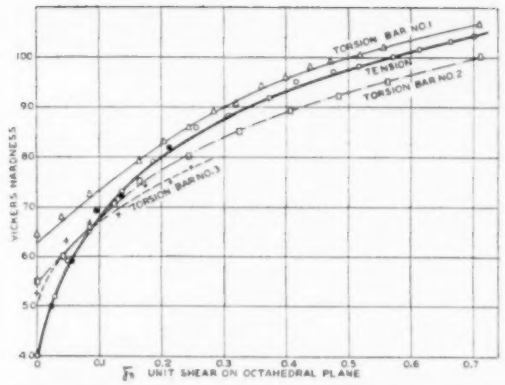

FIG. 4. The hardness of cold-worked copper. ○—tension; ●—compression; Δ—torsion bar no. 1; □—torsion bar no. 2; +—torsion barno. 3. (Letter with bar is used in place of bold face in text.)

observations of such a heterogeneous nature can scarcely be expected on account of the uncertainties involved in surface hardness measurements.

Fig. 5 shows the shearing stress τ_n plotted against the shear γ_n for the tension, compression and for two torsion tests. For values smaller than $\gamma_n=0.2$ the corresponding curves coincide well with a common "strain-hardening curve" $\tau_n=f(\gamma_n)$ which would be characteristic for a metal. When γ_n increases beyond 0.2 the curves tend however, to separate distinctly, but even when $\gamma_n=0.6$ (which would correspond to more than 50 percent elongation in tension) the curves for tension and for torsion do not depart farther than 10 percent of the values of the averaging function.

It should be noted, that when strains become larger ($\gamma_n>0.4$) and particularly when plastic deformations are increased to the extremely large values which can be produced by twisting a copper bar till rupture or by rolling a sheet or drawing a wire down to large reductions of thickness, the preferred orientation of the directions and planes of slip within the crystal grains must produce quite new effects. The anisotropy of the structure and of the mechanical properties of a metal which has been cold worked so much would have to be included in the consideration if further efforts are made to describe quantitatively conditions for such large plastic deformation. It is well known, however, to the practical engineer that the residual stresses produced in the microstructure of the grains and also within cross sections of stressed bodies under such circumstance make it undesirable to apply such excessive amounts of cold work without annealing. The cold work $\gamma_n>0.5$ is therefore not of great practical importance. It must also be noted that the type of anisotropy produced in a cylindrical rod after drawing through a die and in a flat sheet after severe rolling must considerably differ from each other, as well as the systems of strains which result after these operations.

There is finally another point which needs to be emphasized. It is known that the character of the stress-strain curve is changed when the sign of the cold working stress is reversed. If a bar is stretched in tension and then subsequently tested in compression, "Bauschinger's effect" (lowering of the new yield stress) appears. The same is true when a bar is twisted in one direction and then twisted permanently in

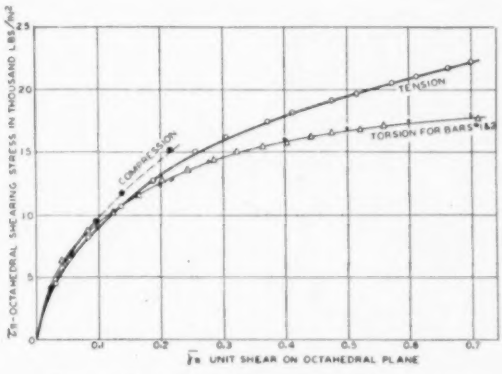

FIG. 5. Strain-hardening curves for copper. ○—tension; ●—compression; Δ—torsion for bar no. 1; +—torsion for bar no. 2. (Letter with bar is used in place of bold face in text.)

the reversed direction, etc. Any change in the type of stress distribution has the same effect of rounding off the sharp break of the stress-strain curve in the next loading curve. The cases of reversed stress in cold working a metal need a further analysis, for example what effect the cold working of a bar by tension will have when it is used in compression and vice versa.

The various experiments which have been quoted and the results of the comparative tests on the cold working of copper may perhaps be summed up by stating that for not too large deformations, cold working of a metal may be described by the curve connecting the octahedral shearing stress with the corresponding shear.

Dielectric Loss Measurements Parallel to Laminations*

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(Received December 16, 1936)

Laminated material is often used as insulation in an electrical device in such a way that a large component of the dielectric field passes through it parallel to its laminations. In present test methods dielectric loss measurements are made on such material with the dielectric field passing through it perpendicular to its lamination. It is evident that the two conditions are different and the dielectric losses as measured by test are not the same as exist when in use. This paper presents a test method by which power factor, dielectric constant and dielectric loss factor of laminated insulating materials can be measured with the dielectric field parallel to the laminations. Results of measurements made with the dielectric field parallel to laminations of both unconditioned and conditioned specimens are compared, respectively, with results obtained with the field perpendicular to laminations.

INTRODUCTION

IT is common practice that measurements of power factor and dielectric constant of solid plate insulating materials be made between lead-foil electrodes symmetrically placed on its surfaces. In the case of laminated insulating materials, these measurements are accordingly made with the dielectric field perpendicular to the laminations. However, in many uses of these materials as insulation, they are placed in such a position that existing alternating dielectric fields pass through them parallel to their laminations. This condition exists when such insulation is used in radio condensers, metal radio tubes, radio tube sockets, terminal blocks, etc. This means that these materials are used in an entirely different manner from which they were tested.

Dielectric losses of homogeneous insulating materials such as quartz, Isolantite, hard rubber, Pyralin, etc., are independent of the direction in which the dielectric field passes through them. In the case of heterogeneous materials, however, such as laminated phenolics, the direction of the field relative to laminations has a big effect on the measured power factor, dielectric constant and hence dielectric loss factor of the material. Materials such as laminated phenolics are composed of alternate layers of varnish impregnated paper and pure varnish, two materials of different dielectric properties. Power factor, dielectric constant and dielectric loss factor of a series combination of these two dielectrics, such as exists when the dielectric field is perpendicular to laminations, are different, respectively, from a parallel combination of these two layers, as exists when the dielectric field is parallel to laminations.

The work described in this paper was undertaken to develop a satisfactory test method by which power factor, dielectric constant and dielectric loss factor could be measured parallel to laminations of laminated insulation. The materials studied were Phenolite (trade name for National Vulcanized Fibre Company's laminated phenolic products), DuPont Pyralin and hard rubber.

APPARATUS

The condenser in which the dielectric materials were tested was a simple parallel plate capacitor. Its plates were heavy brass disks, 7.92 inches in diameter whose faces were carefully machined and ground to absolute flatness. These plates were made quite heavy so that they would not warp. Their backs were machined in three steps, so that they were 1 inch thick at the center for a 2 inch diameter, $\frac{13}{16}$ inch thick for an additional $1\frac{1}{2}$ inch radius, then reduced to $\frac{1}{2}$ inch thick at the outer rim. To prevent the formation of undesirable surface oxides the plates were chromium plated.

One plate was held in a horizontal position with the smooth flat surface up, rigidly and

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electrically connected to its surrounding shield. On its face, near the outer rim, were placed three quartz insulating rods, 0.225 inch in diameter. The faces of these insulating spacers were ground parallel to each other and their heights did not differ by more than 0.2 mil, as measured with a machinist's micrometer. On these quartz spacers rested the upper disk plate to form a parallel plate capacitor. The shield enclosing the capacitor was in the form of a box $10\times10\times5$ inches high made of $\frac{1}{16}$ inch thick aluminum. The leads to the two plates of the capacitor were $\frac{1}{4}$ inch diameter chromium plated brass rods screwed into tapped holes in the center of the disks. A lead amalgam was wiped on the threads to insure good electrical contact.

The lead from the top capacitor plate was so shaped that it passed through a $\frac{3}{4}$ inch hole in the lid drilled about one inch from the edge. Connection between this test capacitor and the paralleling standard capacitor was made by a three inch long conductor attached to the standard capacitor and terminating in a hole containing mercury which was drilled in the end of the $\frac{1}{4}$ inch brass lead.

Because the two disks of the capacitor were made heavy, it was assumed that their sagging was negligible and their separation was taken equal to the height of the insulating quartz spacers.

Procedure

To determine power factor and dielectric constant parallel to the laminations of laminated dielectrics, it was necessary to have the dielectric field pass through the specimens parallel to laminations during the test. This was accomplished by cutting specimens with a smooth circular saw in the form of strips $5\frac{1}{4}$ inches long and 0.240 inch wide by the thickness of the material and then inserting them between the plates of the parallel plate capacitor.

Because the average height of the specimens and the total area of the lower plate covered by the specimens must be known, the width, thickness and length of a representative number were measured. The total area of the lower plate covered by the specimens was computed by multiplying the number of strips by the average area covered by one strip.

With the capacitor insulated by 0.2619 inch high spacers it was possible to insert the 0.240 inch high strips between the plates resting on their sawed edges. Since the capacitor consisted of parallel plates the dielectric field set up between them was perpendicular to their faces, and further, since the specimens were resting on their sawed edges the dielectric field passed through them parallel to their lamination. Fig. 2 is a cross-sectional view of the capacitor with the dielectric material under test.

The manipulation of the electrical circuit to make the measurements will be discussed with reference to the circuit shown in Fig. 1. With C_x, the parallel plate test capacitor, connected in parallel with C, which is set at approximately its minimum capacitance, the circuit is roughly tuned by C_L. Resonance is then obtained by adjusting C, obtaining capacitance C_1. C_x is then

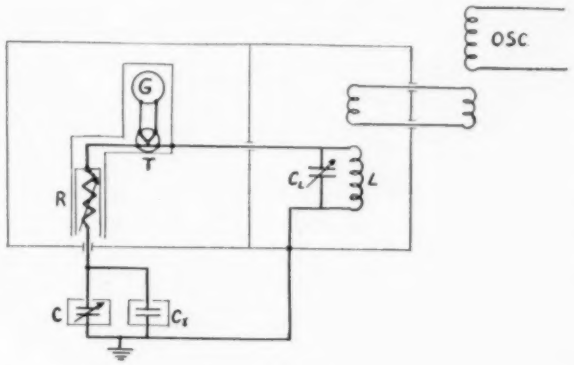

Fig. 1.

disconnected from C, and the circuit again tuned by C, obtaining capacitance C_2. Resistance R_2 is added until the galvanometer deflection with C alone in the circuit equals that when C and C_x were connected in parallel.

The equivalent electrical circuit of the capacitor with the dielectric material under test is shown in Fig. 3. It consists of the loss-free parallel air capacitance C_p connected in parallel with another branch consisting of the loss-free series air capacitance C_s in series with the dielectric material under test, which is represented by a series combination of a loss free capacitance C and a pure resistance R. The quartz insulating spacers are not represented on this equivalent electrical circuit because their extremely low power losses were negligible.

TABLE I. *Power factor, dielectric constant and dielectric loss factor of $\frac{1}{8}$ inch thick disk plate specimens determined with lead-foil electrodes and by the capacitor method at different plate spacings. All measurements perpendicular to laminations.*

Specimens	Lead-foil Electrodes			Parallel Plate Capacitor Method								
				0.1390" Spacing			0.1472" Spacing			0.1588" Spacing		
	PF	K	LF	PF	K	LF	PF	K	LF	PF	K	LF
Phenolite Spec. A–794	0.0240	3.69	0.089	0.0234	3.63	0.085	0.0232	3.66	0.085	0.0231	3.66	0.085
Phenolite Spec. A–805	.0357	4.25	.152	.0349	4.25	.149	.0348	4.28	.149	.0348	4.28	.149
Phenolite Spec. A–793	.0389	4.33	.168	.0382	4.27	.163	.0383	4.27	.163	.0380	4.29	.164
Phenolite Spec. A–817	.0595	5.06	.300	.0575	4.94	.284	.0572	4.97	.284	.0573	5.01	.287
Hard Rubber Spec. O–202	.0076	2.87	.022	.0073	2.76	.020	.0072	2.78	.020	.0071	2.78	.020
Pyralin Spec. O–207	.0500	6.06	.303	.0493	6.04	.298	.0491	6.08	.298	.0490	6.11	.299

The capacitance C_a of the air gap in series with the dielectric specimens in the capacitor is computed by the following approximate relation.

$$C_a = 0.225A/(d-t), \tag{1}$$

in which A = the area of the dielectric specimens (sq. in.) covering the bottom plate,
t = average height of specimens (inch),
d = height of insulating spacers (inch).

The value of the parallel air capacitance C_p is determined from the following:

$$C_p = C_e - 0.225A/d, \tag{2}$$

where C_e is the equivalent series capacitance of the test capacitor when it does not contain any solid dielectric material other than its quartz spacers.

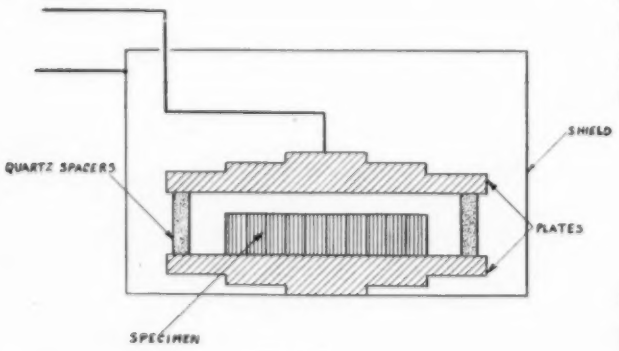

FIG. 2.

The equivalent series resistance R and capacitance C of the dielectric specimens are computed from these relations

$$R = R_t\left(\frac{C_t}{C_t - C_p}\right)^2 = R_2\left(\frac{C_2}{C_t - C_p}\right)^2, \tag{3}$$

$$C = \frac{C_a(C_t - C_p)}{C_a - (C_t - C_p)}, \tag{4}$$

and the power factor at 1000 kc.

$$\mathrm{PF} = 6.28 \times 10^{-6} RC, \tag{5}$$

where R is in ohms and C in micro-microfarads, and the dielectric constant by this approximate relation

$$K = Ct/0.225A. \tag{6}$$

When dielectrics are compared which have different dielectric constants, a knowledge of their loss factor (LF) is more important than their power factor. It is expressed as the product of power factor and dielectric constant.

$$\mathrm{LF} = K \times \mathrm{PF}. \tag{7}$$

Discussion of Method

Before this method of test is discussed with reference to its use for measuring power factor and dielectric constant parallel to laminations, the effect of such variables as plate spacings,

TABLE II. *Power factor, dielectric constant and dielectric loss factor of 5¼ inch square, one-piece and compound specimens, perpendicular and parallel to laminations determined by capacitor method at different plate spacing.*

Specimens	Shape of Specimen	Diel. Field Rel. to Lam.	Parallel Plate Capacitor Method								
			0.1390" Spacing			0.1472" Spacing			0.1588" Spacing		
			PF	K	LF	PF	K	LF	PF	K	LF
Phenolite Spec. A–741	5¼" sq.	Perp.	0.0235	3.73	0.088	0.0236	3.76	0.089	0.0237	3.78	0.090
Phenolite Spec. A–825	5¼" sq.	Perp.	.0617	5.64	.348	.0619	5.66	.351	.0627	5.77	.362
Phenolite Fiber Comb. Spec. O–210	5¼" sq.	Perp.	.0605	6.12	.371	.0610	6.25	.381	.0615	6.29	.387
Hard Rubber Spec. O–202A	5¼" sq.	Perp.	.0072	2.78	.020	.0073	2.80	.020	.0073	2.81	.021
Pyralin Spec. O–207A	5¼" sq.	Perp.	.0491	6.06	.297	.0488	6.10	.298	.0493	6.22	.306
Phenolite Spec. 7A	Strips	Perp.	.0343	4.20	.144	.0345	4.23	.146	.0346	4.25	.147
Phenolite Spec. 10A	Strips	Perp.	.0390	4.31	.169	.0391	4.35	.170	.0394	4.38	.173
Phenolite Spec. 4A	Strips	Perp.	.0532	5.67	.302	.0534	5.69	.305	.0538	5.81	.313
Phenolite Spec. 16A	Strips	Para.	.0432	4.18	.181	.0433	4.21	.183	.0435	4.24	.185
Phenolite Spec. 7B	Strips	Para.	.0545	4.82	.263	.0552	4.87	.269	.0555	4.93	.273
Phenolite Spec. 9C	Strips	Para.	.0572	4.94	.283	.0579	5.00	.289	.0585	5.08	.298

area and kind of specimen tested, will be considered. A comparison is drawn between measurements made by this capacitor method and by the method of providing the specimens with lead-foil electrodes.

In Table I are listed comparative data of results made by first testing the same ⅛ inch thick six inch disk specimen perpendicular to laminations in the capacitor and then when provided with lead-foil electrodes. In the calculations, the fringing of the dielectric field along the periphery of the 4½ inch diameter lead-foil electrodes was taken into account.

Also listed in Table I are the results of measurements obtained by testing the ⅛ inch thick six inch diameter disk specimens by the capacitor method at three different plate spacings, 0.1390 in., 0.1472 in. and 0.1588 in. The results for all three spacings show very good agreement among themselves, indicating that within the accuracy of the method the calculated results of power factor, dielectric constant and dielectric loss factor are independent of plate spacing. This fact applies equally well for homogeneous dielectrics such as Pyralin and hard rubber as for heterogeneous laminated phenolics.

The data tabulated in Table II were obtained by testing in the capacitor at the three plate spacings, one-piece 5¼ inch square specimens and strip specimens arranged to form 5¼ inch squares. Some strip specimens were tested parallel to laminations while others were tested perpendicular to laminations. The results show a slight tendency to increase with plate spacing, illustrating that with square specimens the computed results are not entirely independent of the

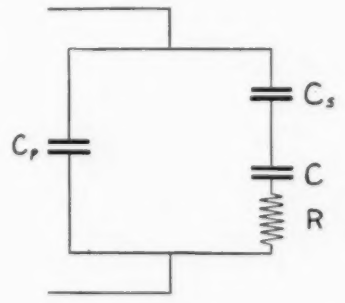

FIG. 3.

TABLE III. *Power factor, dielectric constant, and dielectric loss factor with field perpendicular and parallel to laminations of unconditioned specimens. All tests made by the parallel plate capacitor method.*

SPECIMENS	SHAPE OF SPECIMENS	DIELEC. FIELD REL. TO LAM.	POWER FACTOR	DIELEC. CONST.	DIEL. LOSS FACTOR
Phenolite Spec. A–833	5¼ inch square	perpendicular	0.0274	3.90	0.107
	strips para. to paper grain	perpendicular	.0278	3.91	.109
	" " " " "	parallel	.0488	4.41	.215
	" perp. " " "	perpendicular	.0276	3.89	.108
	" " " " "	parallel	.0538	4.68	.252
Phenolite Spec. A–831	5¼ inch square	perpendicular	.0348	4.29	.149
	strips para. to paper grain	perpendicular	.0346	4.26	.147
	" " " " "	parallel	.0520	4.86	.253
	" perp. " " "	perpendicular	.0349	4.25	.149
	" " " " "	parallel	.0575	4.95	.285
Phenolite Spec. A–817	5¼ inch square	perpendicular	.0558	4.83	.270
	strips para. to paper grain	perpendicular	.0559	4.82	.270
	" " " " "	parallel	.0730	5.48	.400
	" perp " " "	perpendicular	.0560	4.80	.269
	" " " " "	parallel	.0781	5.80	.453
Hard Rubber Spec. O–202	5¼ inch square	perp. to faces	.0073	2.80	.020
	strips	perp. to faces	.0072	2.78	.021
	strips	para. to faces	.0074	2.81	.021
Pyralin Spec. O–207	5¼ inch square	perp. to faces	.0492	6.10	.303
	strips	perp. to faces	.0490	6.04	.296
	strips	para. to faces	.0490	6.08	.298

spacing of the capacitor plates. This slight increase is probably caused by fraying of the dielectric field which tends to concentrate at the corners of the specimen. As the separation of the plates is increased this fraying becomes more pronounced, with the consequence that the losses are slightly higher. In the most severe case noted, however, the change in dielectric loss factor for the two spacings 0.1390 in. and 0.1588 in. amounted to only 0.016, or 4 percent, a negligible amount for this type of testing. However, to have all values comparable the capacitor plates were separated by 0.1472 inch high spacers when $\frac{1}{8}$ inch thick materials were tested perpendicular to laminations and by 0.2619 inch high quartz spacers when 0.240 inch high strip specimens were tested parallel to laminations.

The independence of uniformity of the dielectric field between specimen and upper plate, on the computed values, is shown by the results obtained on specimen No. O–210 and on those tested parallel to laminations. These results showed the same small variations with spacing of the capacitor plates, as did homogeneous dielectrics such as Pyralin and hard rubber which have a uniform dielectric field between them and the upper plate. Specimen No. O–210 was composed of Phenolite strips 5¼ inch long of $\frac{1}{8}$ inch square cross section having a dielectric constant of 3.6 alternated with strips of equal dimensions of hard fiber, having a dielectric constant of 8.1. There were twenty strips of each, Phenolite and hard fiber, giving a specimen approximately 5¼ inch square.

For testing specimens composed of parts, as the strips in the above Phenolite-hard fiber combination, it is necessary that they be laid close together so that no appreciable air spaces are between them. Tests made on thirty strips, similar to those above, showed that if air spaces were between the strips the computed results of power factor, dielectric constant, and dielectric loss factor were higher than when no spaces were between them. For instance, with an average spacing of $\frac{1}{32}$ inch between each of the thirty strips, the dielectric loss factor was about 4 percent higher than when they were close together. This change is probably also caused by a fraying of the dielectric field which concentrates at the corners of the individual strips. When strip specimens are laid closely together the computed results are the same as for a one-piece specimen. This is shown by the results of Table III, where it is seen that the computed

TABLE IV. *Power factor, dielectric constant, and dielectric loss factor of Phenolite specimens No. 14 and No. 15. Strip specimens cut both perpendicular and parallel to paper grain. Conditioned at 90 percent relative humidity at 37°C.*

	Lead-foil Electrode Method*			Parallel Plate Capacitor Method**											
				Strips Cut Perp. to Paper Grain						Strips Cut Para. to Paper Grain					
	Field Perp. to Lam.			Field Perp. to Lam.			Field Para. to Lam.			Field Perp. to Lam.			Field Para. to Lam.		
Days Cond.	PF	K	LF	PF	K	LF	PF	K	LF	PF	K	LF	PF	K	LF
0	0.0214	3.59	0.077	0.0210	3.58	0.075	0.0349	3.86	0.135	0.0211	3.57	0.075	0.0325	3.76	0.122
4	.0220	3.72	.082	.0282	4.06	.114	.0887	5.34	.474	.0252	3.91	.100	.0584	4.58	.267
11	.0242	3.74	.091	.0331	4.12	.136	.1210	5.54	.670	.0275	3.97	.110	.0802	5.04	.404
30	.0257	3.97	.106	.0343	4.20	.146	.1281	5.66	.718	.0298	4.20	.123	.0922	5.20	.558
64	.0286	4.10	.117	.0350	4.35	.152	.1310	5.86	.767	.0333	4.31	.143	.1085	5.54	.600
	Phenolite Specimen No. 15														
0	.0270	3.90	.105	.0266	3.89	.103	.0460	4.32	.198	.0264	3.88	.102	.0404	4.14	.168
4	.0281	3.91	.110	.0506	4.98	.253	.1590	7.02	1.112	.0446	4.70	.210	.1041	6.02	.625
11	.0292	3.92	.115	.0574	5.29	.308	.1912	7.36	1.413	.0586	5.06	.296	.1620	6.74	1.090
30	.0300	4.33	.135	.0592	5.31	.310	.2124	7.81	1.691	.0617	5.11	.322	.1749	7.05	1.310
64	.0308	4.67	.177	.0635	5.33	.338	.2255	8.58	1.930	.0634	5.28	.335	.1818	7.66	1.400

* Samples $5\frac{1}{4} \times 5\frac{1}{4} \times \frac{1}{4}$" thick.
** Samples $5\frac{1}{4} \times 0.240 \times \frac{1}{4}$" thick—40 strips.

values are the same for specimens composed of strips as for the one-piece square specimens.

Specimens having areas of approximately 27 square inches were used so that appreciable readings of the condenser and resistor could be obtained. Tests made, however, on square specimens of smaller areas gave results slightly lower. For instance, the dielectric loss factor of a specimen of 16 square inches was approximately 3 percent lower than that obtained for a square specimen of 27 square inches.

Experimental Results

Unconditioned specimens

In Table III are listed the results of measurements made on various materials with the dielectric field perpendicular to laminations and in the two parallel-to-lamination directions, namely perpendicular and parallel to the paper grain. The results show that dielectric losses are about 100 percent higher parallel to laminations than they are perpendicular to them. This is accounted for by the fact that in the parallel-to-lamination directions, the varnish impregnated paper layers are in parallel with the resin layers, while in the perpendicular-to-lamination direction they are in series.

The dielectric losses in the two parallel-to-lamination directions are different. The dielectric loss factor obtained on strip specimens cut perpendicular to the paper grain is about 15 percent higher than that obtained on similar strip specimens cut along the paper grain. This difference can be explained by considering the physical positions of the cellulosic fibers in the strip specimens. When strip specimens, cut perpendicular to the grain, are tested parallel to laminations, the cellulosic fibers of the paper appear as small standing columns in parallel with the solid phenolic resin. On the other hand, when strip specimens cut along the paper grain, are tested parallel to laminations, the cellulosic fibers of the paper appear as lying perpendicular to the dielectric field and in series with solid phenolic resin, which penetrated into the paper between the fibers.

The results also showed that dielectric losses of homogeneous dielectrics such as Pyralin and hard rubber are independent of the direction the dielectric field passes through them.

Conditioned specimens

In many climates where dielectric materials are used the relative humidity exceeds 90 percent for long periods of time, hence a knowledge of their insulating qualities, under these humid conditions, is much more important than those

under dry conditions. To determine the effect of absorbed moisture on the dielectric losses of Phenolite, strip specimens were conditioned in humid atmosphere maintained at 90 percent relative humidity at 37°C, and also by total immersion in water at 25°C. The shape of the specimens tested and the procedure of test followed, were the same as for the unconditioned specimens. To get a knowledge of the variation of power factor, dielectric constant and dielectric loss factor of the specimens with time of exposure to these conditions, they were withdrawn from their conditioning chambers and tested periodically. Since laminated phenolic materials swell, when they absorb moisture the dimensions of the specimens had to be remeasured each time they were tested.

In Table IV are listed the test data for two Phenolite plates, Nos. 14 and 15, humidified at 90 percent relative humidity at 37°C, with strips cut both perpendicular and parallel to the grain of the paper. In the first group of three columns are the results obtained from testing square specimens provided with lead-foil electrodes. The second and third groups of three columns each, are the data obtained by testing strip specimens cut perpendicular to the grain of the paper in the parallel plate capacitor. The second group of three columns gives the results of measurements made with the field parallel to laminations. The fourth and fifth groups of three columns each cover similar data obtained on strip specimens cut parallel to the paper grain. The variation of the dielectric loss factor of Phenolite specimen No. 15, with time of conditioning at 90 percent relative humidity at 37°C, is shown in Fig. 4.

It is to be particularly noticed that power factor, dielectric constant and dielectric loss factor perpendicular to laminations are not the same for the conditioned strip specimens as they are for the conditioned square specimens, which were tested with lead-foil electrodes. This is due to the fact that in the case of strip specimens there is a much larger surface exposed to the humid air than in the case of the one piece $5\frac{1}{4}$ inch square specimen, with the result that the strip specimens will take up much more moisture for short time exposures. Hence, when the strip specimens are tested between the capacitor

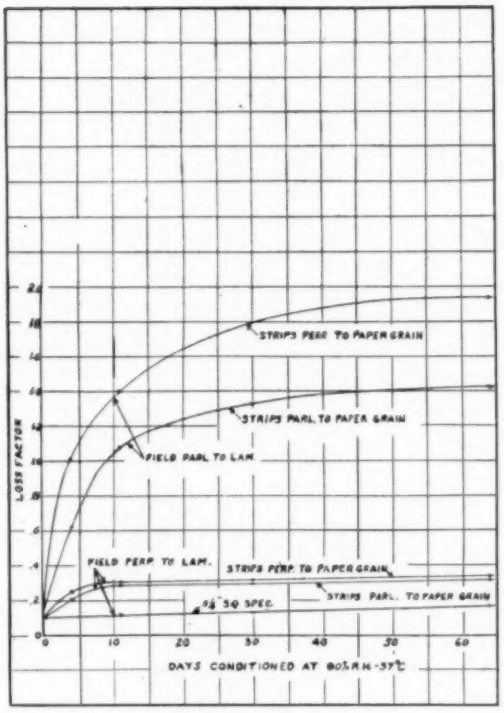

FIG. 4. Phenolite specimen No. 15.

plates, there is much more moisture in the dielectric field than when the one-piece square specimen is tested with lead-foil electrodes. The consequence is that the dielectric losses of the strip specimens will be higher than those of the one-piece specimen.

The exceptionally high dielectric losses parallel to laminations of conditioned strip specimens, are due primarily to the fact that the outside surfaces of the strip specimens become saturated with water, even at moderate conditioning. These saturated surfaces may have a power factor and dielectric loss factor as high as 0.50 and 4.0, respectively, as determined by testing totally saturated specimens. Hence, when conditioned strip specimens are tested with the dielectric field parallel to their laminations, these extremely high loss outer layers are placed in parallel with the dry low loss middle portions and cause the over-all power factor, dielectric constant and dielectric loss factor to be very high. Whereas, when the same strip specimens are tested perpendicular to laminations, these high loss outer layers are in series with the low loss middle portions.

In Table V are listed test results illustrating

TABLE V. *Power factor, dielectric constant and dielectric loss factor of Phenolite specimen No. 677. Comparison between conditioning at 90 percent relative humidity at 37°C and by immersion in water at 25°C.*

	Conditioned at 90% Rel. Humidity at 37°C						Conditioned in Water at 25°C					
	Lead-foil Electrodes*			Para. Plate Capacitor**			Lead-foil Electrodes*			Para. Plate Capacitor**		
	Field Perp. to Lam.			Field Para. to Lam.			Field Perp. to Lam.			Field Para. to Lam.		
Days Cond.	PF	K	LF	PF	K	LF	PF	K	LF	PF	K	LF
0	0.0232	3.83	0.089	0.0349	3.71	0.130	0.0230	3.82	0.088	0.0350	3.71	0.131
5	.0399	4.21	.168	.0971	5.10	.525	.0497	4.26	.212	.2080	5.77	1.201
10	.0464	4.53	.210	.1490	5.71	.804	.0630	4.70	.296	.3030	7.14	2.160
21	.0600	5.00	.300	.2281	6.64	1.532	.0748	5.02	.375	.3710	8.82	3.280
30	.0663	5.16	.342	.2324	7.05	1.672	.0752	5.16	.388	.4012	9.60	3.850
48	.0668	5.37	.359	.2441	7.55	1.782	.0760	5.27	.401	.4061	10.30	4.182

* Samples $5\frac{1}{2} \times 5\frac{1}{2} \times \frac{1}{8}$".
** Samples $5\frac{1}{4} \times 0.240 \times \frac{1}{8}$"—40 strips.

the comparative effect of conditioning Phenolite specimen No. 677 at high humidity and by total immersion. This table includes data obtained by testing square specimens provided with lead-foil electrodes perpendicular to laminations, together with results made on strip specimens with the dielectric field parallel to laminations. The variation of the dielectric loss factor of Phenolite specimen No. 677, with the dielectric field perpendicular and parallel to laminations, with time of conditioning at 90 percent relative humidity at 37°C, and by immersion in water at 25°C is shown in Fig. 5.

Hypothetical Dielectric

The difference in the dielectric properties of unconditioned laminated insulation in the three directions considered above, are accounted for mathematically in the following discussion of a hypothetical dielectric. This dielectric is designed to approximate the physical make-up of laminated phenolic materials whose paper layers are impregnated with and bound together by solid phenolic resin. This hypothetical dielectric consists then of two different dielectric materials; one resembling the cellulose of paper and the other resembling the solid phenolic resin of laminated phenolics.

The dielectric matter which represents the cellulosic fibers of paper is assumed to be in the form of rods of square cross section. These rods lie parallel to each other so as to resemble the position of the cellulosic fibers of paper, the majority of which, in most papers, lie parallel to the grain of the paper. These rods are arbitrarily assumed to have a square cross section of 0.050 inch per side. The rods are considered as being in layers with a separation of 0.005 inch between rods in a layer and with a separation of 0.030 inch between layers. For simplicity the rods of each layer are considered to be in alignment.

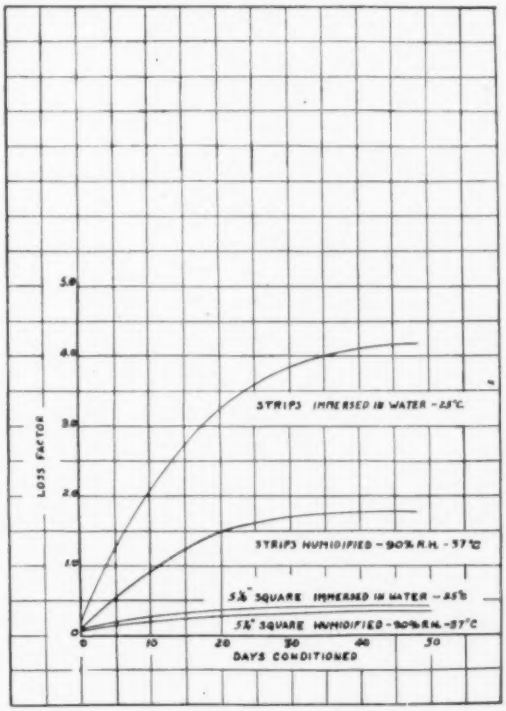
LOSS FACTOR
STRIPS IMMERSED IN WATER - 25°C
STRIPS HUMIDIFIED - 90% R.H. - 37°C
5½" SQUARE IMMERSED IN WATER - 25°C
5½" SQUARE HUMIDIFIED - 90% R.H. - 37°C
DAYS CONDITIONED

Fig. 5. Phenolite specimen No. 677.

The space between the rods in a layer and the space between layers is assumed to be completely filled with a dielectric material, which is to resemble the solid phenolic resin in laminated phenolic materials. The dielectric matter which fills the 0.005 inch spacing between the rods of a layer of this hypothetical dielectric resembles the solid resin that penetrated into the spaces between the fibers of the base paper of the laminated phenolic material. The dielectric matter which fills the 0.030 inch spacing between layers of the rods corresponds with the film of solid resin between the paper layers or laminations of the phenolic products.

The direction which is perpendicular to the layers of these rods is taken as the perpendicular-to-lamination direction. There are two distinct formations of these rods when this hypothetical dielectric is considered in the two parallel-to-lamination directions. In one case, the solid rods are in parallel with the other dielectric material of the hypothetical dielectric, resembling the relative positions of the cellulosic fibers and solid phenolic resin in the strip specimens cut perpendicular to the paper grain, while in the other parallel-to-lamination direction, the rods are both in series and in parallel with the other dielectric material, as are the cellulosic fibers and solid phenolic resin in the strip-specimens cut parallel to the paper grain.

The solid rods of this hypothetical dielectric are assumed to have a dielectric constant of 7.0 and a power factor of 0.055, while the solid matter which fills the spaces between them is assumed to have a dielectric constant of 2.0 and a power factor of 0.015.

TABLE VI. *Computed power factor, dielectric constant, and dielectric loss factor of the hypothetical dielectric*

DIRECTION CONSIDERED	POWER FACTOR	DIEL. CONST.	DIEL. LOSS FACTOR
Perp. to Lamination	0.0267	3.45	0.092
Para. to Laminations Perp. to Lgth. of Rods	.0393	4.30	.169
Para. to Laminations Para. to Lgth. of Rods	.0510	4.87	.248

Since this hypothetical heterogeneous dielectric is composed of two dielectrics, whose dimensions and properties are known, equivalent electric circuits for their combinations in three directions can be set up and accordingly, power factor, dielectric constant, and dielectric loss factor computed. The results of these computations are listed in Table VI.

CONCLUSIONS

1. A method is presented for measuring power factor, dielectric constant and hence dielectric loss factor parallel to the laminations of laminated materials.

2. Dielectric losses parallel to laminations of unconditioned laminated phenolic materials are about 100 percent higher than in the perpendicular-to-lamination direction.

3. Dielectric losses parallel to laminations of unconditioned laminated phenolic materials, are about 15 percent higher when the dielectric field is parallel to the paper grain than when it is perpendicular to it.

4. Dielectric losses parallel to laminations of conditioned laminated phenolic materials are as much as ten times the corresponding values in the perpendicular-to-lamination direction.

5. A hypothetical dielectric is presented whose dielectric properties in the three directions very closely approximate those of unconditioned laminated phenolic materials.

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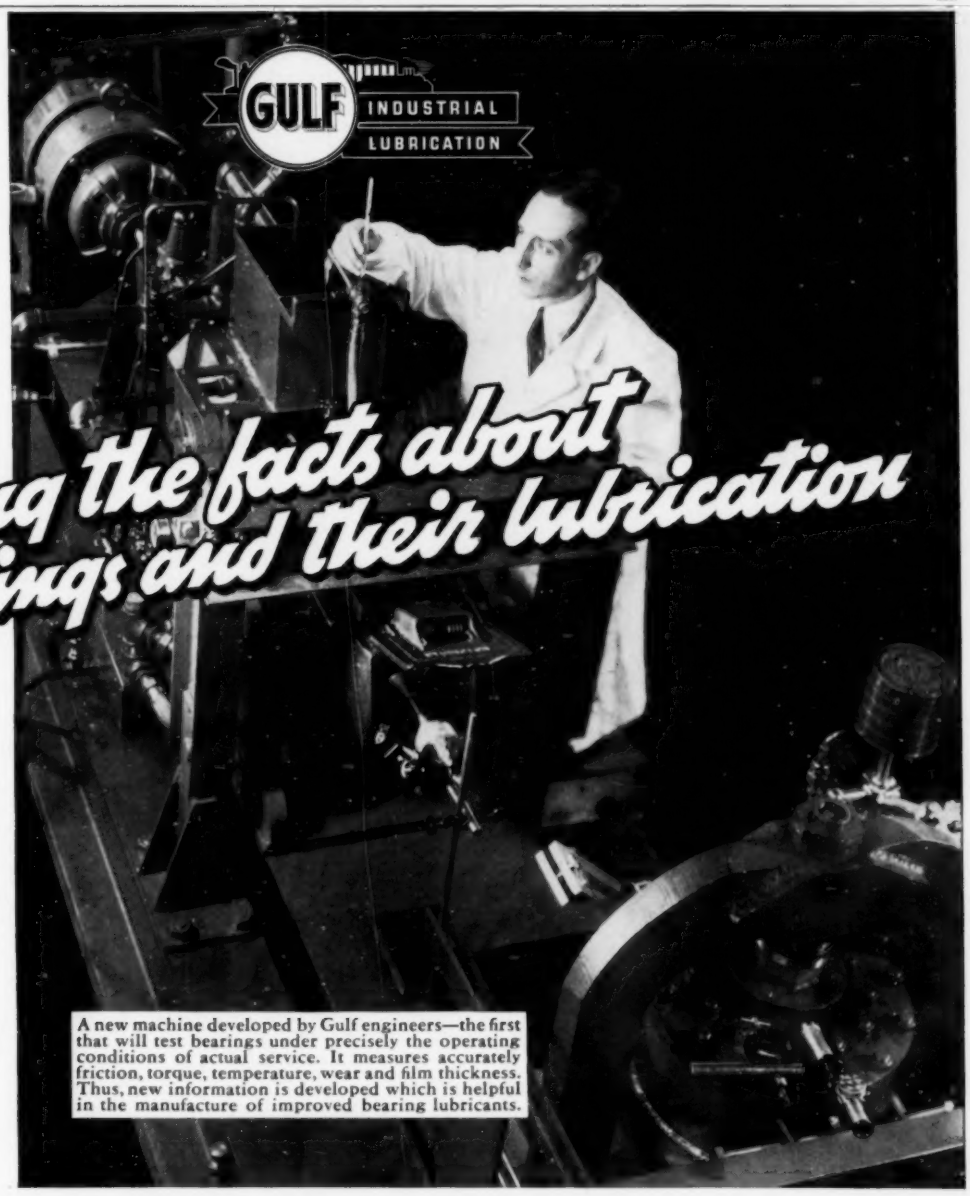
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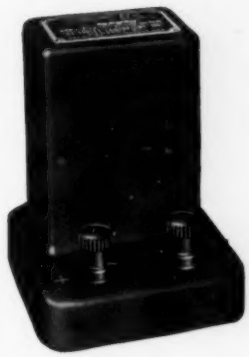

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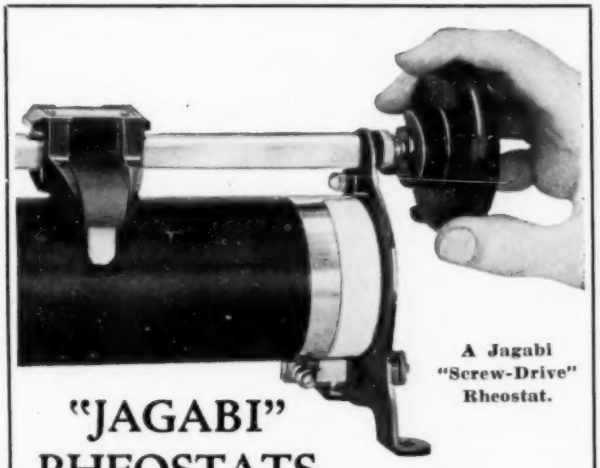

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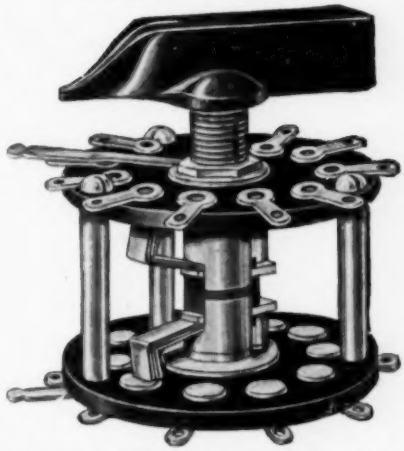

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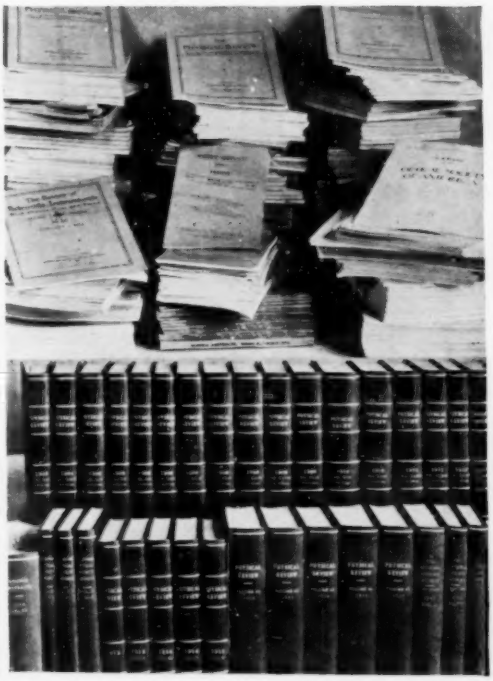

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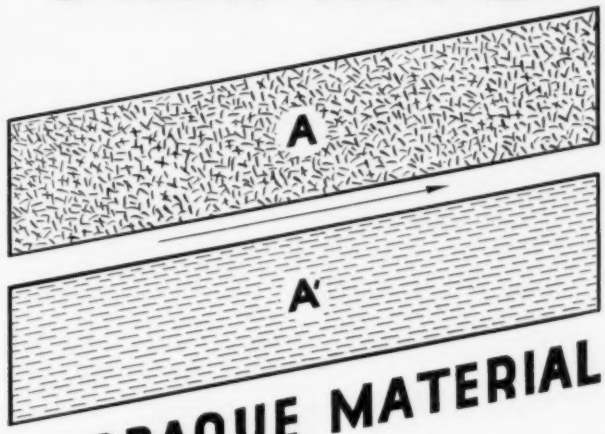

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